MODERN PHOTOGRAPHIC PROCESSING

VOLUME 1

Grant Haist

A volume in the Wiley Series on Photographic Science and Technology and the Graphic Arts, edited by Walter Clark

MODERN PHOTOGRAPHIC PROCESSING is the most complete reference ever published on the chemistry and technology of photographic processing. Volume 1 presents the evolution, theory, and practice of the basic photographic process—the silver image.

In a well-structured, easy-to-follow analysis, Volume 1 examines the fundamental chemical science that has made today's photography possible. The first chapters present the atomic basis of modern photography and the composition of the light-sensitive photographic material. The author then proceeds with a thorough discussion of latent image formation and its amplification by developing agents and other developer ingredients. The mechanism of development is examined, and practical formulas for photographic solutions are given. The book concludes with detailed coverage of techniques for developing (including fine grain, high definition, general purpose, and special purpose formulations), fixing, and image conservation.

This comprehensive introduction to photomaterials and the mechanisms of their exposure and development will be of use not only to photographic scientists, but to all engineers, students, and professional and amateur photographers who want a complete, compact reference on the chemistry of the photographic process.

7810

Volume Two of MODERN PHOTOGRAPHIC PROCESSING deals with the chemistry and technology of complex black-and-white and color processes, including reversal and "instant" processes.

MODERN PHOTOGRAPHIC PROCESSING

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MODERN PHOTOGRAPHIC PROCESSING, Vols. 1 and 2
Grant Haist

Modern Photographic Processing

VOLUME 1

Grant Haist

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To PHYLLIS and LYNNE

who suffered my neglect
during the 10 years
of the preparation of this book

Preface

In less than 150 years photography has progressed from a fortunate chemical discovery to a full-fledged science. Like any science, photography has developed its own language, a jargon that often obscures its fundamentals and applications. Yet, many who must comprehend photographic science as part of their endeavors—engineers, patent attorneys, chemists, journalists, research workers, educators, students, and photographers, to name a few—do not have a lifetime to master this language.

This book is one man's attempt to translate the complexity of photographic processes into the English language, retaining only the minimum of photographic terms that are needed to communicate with other photographic workers. This treatment is neither simple or simplified, because modern photographic science is based on complex atomic and chemical principles, but the result should be more readable and more convenient than the original sources.

The early chapters have been programmed to increase in complexity; those unfamiliar with photographic chemistry should start with the first chapter and proceed from there. Specific photographic terms or relationships have been explained when introduced, but most mathematical relationships have not been included. Everyday words have been used to describe these and other specialized relationships and terms. Obviously, anyone familiar with photographic science should go directly to the chapter containing the subject of interest, but often a review of the basics can be beneficial.

An effort has been made to determine the contributions of the earliest workers in each field, so that the reader can gain perspective on modern-day accomplishments. Our best understanding of the theories of the photographic processes is also provided. Because the advance of photography is made possible by the advance of chemistry, much of this book is related to the chemical basis of photographic science.

Any book on photographic processing is essentially a history of past accomplishments. Numerous references have been given for those who wish to know all the details of these practical efforts. Copies of a reference may be easier to obtain than some may imagine, even though one's nearest library may not have the desired item. Most libraries are members of information networks, and material may be obtained on interlibrary loan. For those who lack the time to search further, I have often included a representative example from a patent or an article, using the original author's words, if suitable.

I wish to express my appreciation to Drs. J. A. Leermakers and W. T. Hanson, Jr., each a former Director of the Kodak Research Laboratory, for their support during the preparation of this book. I am also grateful for the continued encouragement of Dr. Walter Clark, Editor of the Wiley Series on Photographic Science and Technology and the Graphic Arts.

Without all those writers who have published their photographic findings, and without that magnificent archive, the Library of the Kodak Research Laboratories, this book could never have been written. Original sources of all references were consulted in the original language, except that translations were used for Japanese and Russian sources.

I am indebted to Mrs. Elizabeth Kraus, Research Associate, and Wilma Kujawski, Head Librarian, for the use of the extensive resources of the Library. Especial acknowledgement is made for the assistance of Mrs. Catherine Clark in securing those almost-lost original historical references and to Miss Shirley Jones for her efforts in obtaining the latest technical literature. I am also indebted to Mrs. Pamela Meyer and Mrs. Martha Stemp for providing the many thousands of patents for my reading.

The editorial suggestions and organization given by Mr. George T. Eaton have contributed immeasurably in the preparation of the final manuscript. He has spent many hours reviewing each chapter as well as preparing the index.

Appreciation is also expressed to my colleagues, Joseph Altman, Charleton Bard, Richard Bent, Chester Berry, Anthony Cavallaro, John Hamilton, James King, Rowland Mowrey, Robert Ross, Keith Stephen, and others who have reviewed certain sections for accuracy of content.

Information contained in this book has been compiled from a variety of sources believed to be reliable and accurate but is not guaranteed to be so. This material is published for information only, and nothing should be construed as recommending any product or practice in violation of any patent or of any law or regulation. It is the user's responsibility to determine the suitability of any material or composition and/or procedure for each purpose, and to adopt such safety precautions and safeguards against toxicity and pollution as may be necessary.

Every effort has been made to prevent errors of fact, but it is inevitable that certain mistakes will be contained in the first printing of a work of this size. Some arbitrary decisions have been made, such as limiting the scope to silver halide photography and passing over certain mathematical concepts that would have been of value for photographic scientists. I would be most interested to learn of any errors of omission or commission, or how this book might be made of greater value in the classroom, darkroom, laboratory, or other areas of use. A letter addressed to the publisher will be most carefully considered.

GRANT HAIST

Rochester, New York
July 1978

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Chapter 1
Atomic Basis of Photography

Photography is essentially a branch of practical chemistry. The materials used and the changes brought about by their agency are all subject to chemical laws.

PAUL N. HASLUCK[21]

The invention of photography was delayed until chemistry could make it possible. As early as 1777 Carl Wilhelm Scheele[1] made the first scientific study of the effect of light on silver chloride. Fifty years earlier Johann Henrich Schulze[1] had used stencils to make light impressions on a mixture of silver nitrate and chalk. The camera obscura—a small darkened box with a lens that cast an image on a ground glass—was an artist's aid widely used during the seventeenth and eighteenth centuries. Both a light-sensitive medium and the camera were available for the invention of photography.

At the beginning of the nineteenth century Thomas Wedgwood, with the help of Humphrey Davy, studied the light sensitivity of silver nitrate but was unsuccessful in making a permanent record of the camera's image. Others claimed to have recorded camera images with silver-sensitized paper but were unable to fix the light impressions. Until the chemistry of the fixing of the fleeting images in silver could be found, photography was only a frustrated hope. And until the powerful amplifying action of certain chemical compounds became known, the early photographic processes of Louis Jacques Mande Daguerre and William Henry Fox Talbot were hopelessly

Figure 1. Photography is possible because of the chemical amplification and chemical fixation of an invisible impression left by light or other radiation. The photographic silver image is revealed to be composed of granular particles that blend to provide the tones of the photograph, as shown in this picture of a kitten (*a*) and in a series of increasing magnification (*b* through *f*) of the silver negative image. (Eastman Kodak Company.)

slow. Even today the chemistry of photographic processes largely determines what can be done with a camera. For this reason a basic understanding of the chemical nature of the atom is essential to an understanding of modern photographic materials and their processing.

All the materials and substances of photography are composed of just three elementary particles: electrons, protons, and neutrons. (See Table 1.) Indeed, all the ordinary matter commonly encountered in this world is composed of just these three particles.[2] Light, on which photography depends, is composed of particlelike photons, which have wave properties as

Figure 1 (*continued*)

Figure 1 (*continued*)

Figure 1 (*continued*)

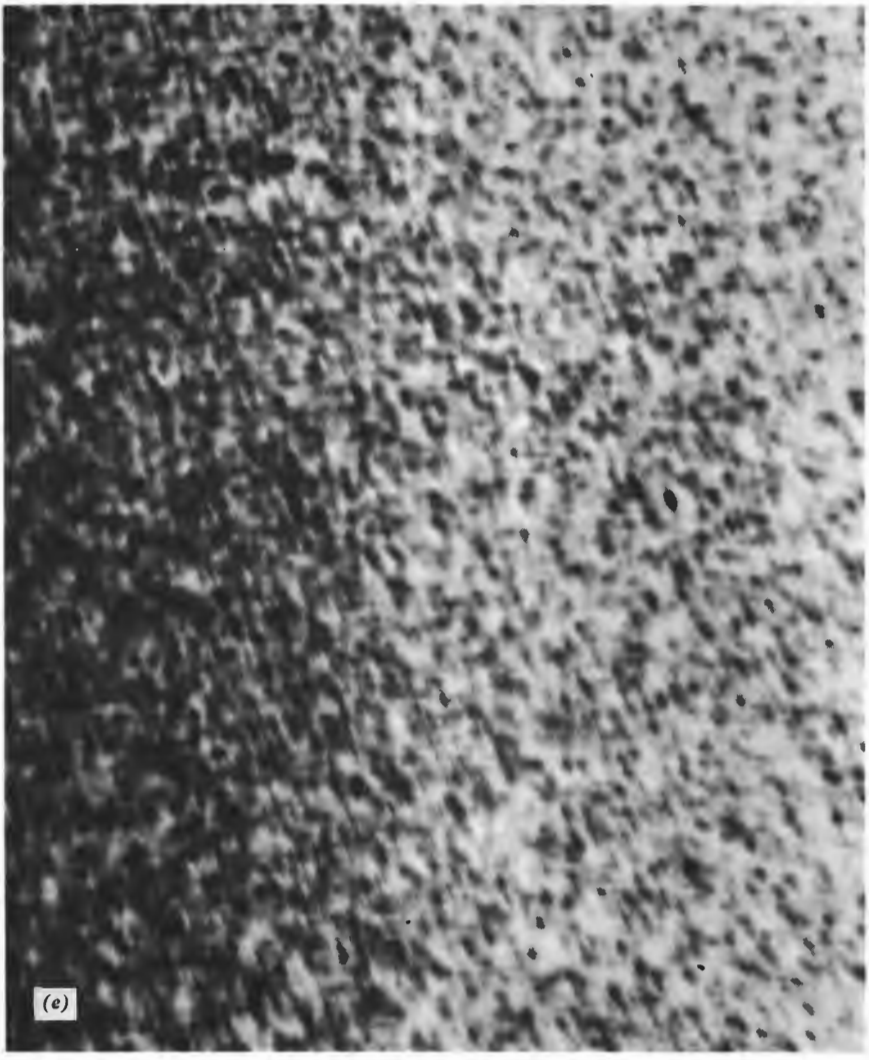

Figure 1 (*continued*)

Figure 1 (*continued*)

Table 1. The Three Particles of Ordinary Matter

Particle	Charge	Mass
Electron	⊖	1
Proton	⊕	1836.1
Neutron	0	1838.6

Mass of neutron and proton based on the mass of the electron taken arbitrarily as 1. *Source*: Based on a chart by Gerald Feinberg, *Sci. Am.*, **216** (5): 132 (1967). [Copyright © 1967 by Scientific American, Inc. All rights reserved.]

well, but are without mass. Some 200 types of elementary particles have been found—most of them only in cosmic ray collisions or in man-made accelerators—but for photographic purposes, only the electron, the proton, and the neutron are relevant.

THE ELEMENTS

Today 106 structural arrangements of electrons, protons, and neutrons are known. These structures, called atoms, cannot be separated into simpler substances by chemical means. Each distinctive atomic structure of this type is called an element. Ninety-two elements are naturally occurring, but only 81 are stable.[3] The existence of the 106th structure has been claimed by different scientific groups,[4] but half the atoms of this element break apart in less than one second. Possibly other atomic structures could be synthesized through the use of a particle accelerator, but these elements would have a short life.[5,6] Once its existence has been established, each element is assigned a name and an atomic number. The atomic numbers increase essentially in the order of increasing atomic weight, but there are a few exceptions.

The names of the elements have been derived from a number of origins, some of them obscure.[7,8] Elements reported before 1800 follow no definite naming scheme. These early names were often derived from Greek or Latin words describing the element's source (for example, calcium comes from *calx*, the Latin noun for limestone) or one of its properties (iodine is derived from *iodes*, the Greek adjective meaning violet colored and descriptive of its

vapor). Other elements were named after gods or goddesses, such as mercury, thorium, cerium, and vanadium.

Since 1800, elements that are metallic in nature have been given names ending in -ium or -um, and nonmetallic elements names ending in -en, -on, or -ine. Recently discovered elements are often named after the place where they were formed. The names berkelium, element 97, and californium, element 98, indicate where these two elements were synthetically prepared. Some elements are named after famous scientists, such as einsteinium (99), fermium (100), mendelevium (101), and nobelium (102).

To simplify the notation, each element is designated by a symbol consisting of one or two letters of the alphabet. The single or first letter is always capitalized. The symbol Ag (from *argentum*, latin for silver) is a short way of saying silver. The symbol for any element may also be used to represent one atomic weight of the element, the number of parts by weight equal to the atomic weight. The parts-by-weight is usually expressed in grams, but any suitable unit may be used. The symbol Ag represents 107.87 g of silver. Table 2 lists the names of 105 elements, their symbols, their atomic numbers, and their atomic weights (if determined).

Table 2. Table of Elements

Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	
Aluminum	Al	13	26.9815
Americium	Am	95	
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	
Barium	Ba	56	137.34
Berkelium	Bk	97	
Beryllium	Be	4	9.01218
Bismuth	Bi	83	208.9806
Boron	B	5	10.81
Bromine	Br	35	79.904
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	

Table 2. *(continued)*

Element	Symbol	Atomic Number	Atomic Weight
Carbon	C	6	12.011
Cerium	Ce	58	140.12
Cesium	Cs	55	132.9055
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.546
Curium	Cm	96	
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	
Fluorine	F	9	18.9984
Francium	Fr	87	
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.9665
Hafnium	Hf	72	178.49
Hahnium	—[a]	105	
Helium	He	2	4.00260
Holmium	Ho	67	164.9303
Hydrogen	H	1	1.0080
Indium	In	49	114.82
Iodine	I	53	126.9045
Iridium	Ir	77	192.22
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanium	La	57	138.9055
Lawrencium	Lr	103	
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.305

Table 2. (*continued*)

Element	Symbol	Atomic Number	Atomic Weight
Manganese	Mn	25	54.9380
Mendelevium	Md	101	
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.179
Neptunium	Np	93	237.0482
Nickel	Ni	28	58.71
Niobium	Nb	41	92.9064
Nitrogen	N	7	14.0067
Nobelium	No	102	
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Plutonium	Pu	94	
Polonium	Po	84	
Potassium	K	19	39.102
Praseodymium	Pr	59	140.0977
Promethium	Pm	61	
Proactinium	Pa	91	231.0359
Radium	Ra	88	226.0254
Radon	Rn	86	
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9055
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	—[a]	104	
Samarium	Sm	62	150.4
Scandium	Sc	21	44.9559
Selenium	Se	34	78.96
Silicon	Si	14	28.086
Silver	Ag	47	107.868
Sodium	Na	11	22.9898

Table 2. *(continued)*

Element	Symbol	Atomic Number	Atomic Weight
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.9479
Technetium	Tc	43	98.9062
Tellurium	Te	52	127.60
Terbium	Tb	65	158.9254
Thallium	Tl	81	204.37
Thorium	Th	90	232.0381
Thulium	Tm	69	168.9342
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten (Wolfram)	W	74	183.85
Uranium	U	92	238.029
Vanadium	V	23	50.9414
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.9059
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

[a] No symbol officially assigned yet.

In the earth's crust, oceans, and atmosphere the element oxygen makes up 46.6% and the element silicon 27.2% of all the matter. Aluminum (8.13%), iron (5.00%), calcium (3.63%), and sodium (2.83%) are next in abundance. Twelve elements constitute 99% of all the earth's matter, leaving only 1% for all the other elements.[7] Fortunately, only a limited number of elements are involved in photographic materials and their processing.

Atomic Number

Each atom of an element may be visualized as a miniature solar system with a compact, central core, called the nucleus, as the sun, and the circling electrons as the planets. The weight of the atom is concentrated in the nucleus, as is all of its positive charge. This charge is supplied by the protons, each possessing

a unit positive charge. The atomic number of the element is equal to—and in fact is derived from—the number of protons in the nucleus.

The nucleus of the first element, hydrogen, contains only one proton, and there is a single electron outside the nucleus. A hydrogen atom has a mass of 0.000 000 000 000 000 000 000 001 662 g (1.662×10^{-24} g), of which the sole electron contributes a rest mass of 0.000 000 000 000 000 000 000 000 000 911 g (9.11×10^{-28} g). The nucleus of the next element, helium, contains two protons and two neutrons. The nucleus of each of the other elements contains both neutrons and protons bound together by strong, short-range forces that are unlike electrostatic or gravitational forces; the nature of these binding forces is not well understood.

The neutron is an uncharged particle of slightly greater weight than the proton. Although a free neutron would spontaneously disintegrate into a proton and an electron with a release of energy, the neutron is *not* composed of a proton and an electron but is in a special state. The electron, as such, does not exist in the nucleus of an atom. The neutron and the proton may be considered to be different states of a particle called a nucleon.[9] A "skin" of neutrons, about 10% as thick as the radius, has been reported to surround the charged core of an atom's nucleus, "something like a horse chestnut."[10]

Atomic Weight

The number of protons and neutrons in the nucleus essentially determines the element's atomic weight, because the electron is only about 1/1800th the weight of the proton or the neutron. But the atoms of an inseparable element may vary slightly in weight because of slight differences in the composition of the nuclei. Atoms of the same element may have been formed by different routes of radioactive decay, giving atomic nuclei of slightly different composition and weight; such atoms are called isotopes. All elements encountered in nature are mixtures of isotopes. The weight of a naturally occurring element is determined by the relative degree of abundance of each isotope, so that the atomic weight is rarely a whole number.

Isotopes have almost identical chemical properties, but different numbers of neutrons are bound to the same number of protons in the nucleus. Most elements have two or more isotopes, but usually one is present in a high percentage and is the main determiner of atomic weight. The atomic weight of an element is usually an irregular number, sometimes known accurately to five or more decimal places. The nearest whole number to the atomic weight is called the mass number; it is also equal to the number of protons plus the number of neutrons in the nucleus. Silver (atomic number 47) has an atomic weight of 107.868. The mass number is 108. There are 47 protons (equal to the atomic number) and 61 neutrons (108 − 47) in the nucleus.

The scale of atomic weights is based on the assignment of a weight of 12.00000 atomic mass units to an isotope of carbon that has an actual weight of 12.00052 and an abundance of 98.893 % of the carbon atoms occurring in nature. The atomic weight of the element carbon is the sum of the products of the atomic mass and the relative abundance of each of the two naturally occurring stable isotopes. Carbon has an atomic weight of 12.011. All other elements are compared to the carbon isotope that has an assigned atomic weight of 12 (exactly). An atomic mass unit is equal to one-twelfth the mass of this isotope of carbon. On this basis, in atomic mass units, the weight of the proton is 1.0072766 and that of the neutron is 1.0086654.

The symbol C represents one atomic weight of the element carbon. The atomic weight of carbon is 12.011 atomic mass units relative to the masses of the other elements. In one atomic weight of carbon, or in the atomic weight of any element, there are 602,209,430,000,000,000,000,000 atoms (that is, more than 600 sextillion). The word "mole" is used to describe this number of atoms of an element, which is also referred to as Avogadro's number (6.02×10^{23}).[11] Dividing this large number into the atomic weight of the element in grams would give the actual weight of each atom. This extremely small number could be used in calculations, but it is much easier to use the atomic weight of a mole, as this is a number larger than one. The mole is the amount of substance that contains as many elementary units as there are carbon atoms in 12 g of carbon-12. The elementary unit may be atoms, molecules, ions, or electrons.[12]

Electronic Nature of the Atom

Atoms of an element are uncharged. The nucleus has a positive charge equal to the number of protons (the atomic number). This positive charge is neutralized by an equal number of electrons of unit negative charge outside of the nucleus. Normally, positive and negative particles would be strongly attracted to each other, and a structure containing them would collapse. But this event may be avoided if the particles are in motion, as they are in atoms. The attractive force drawing the positive protons toward the negative electrons is balanced out by the centrifugal or repulsive force, so that a stable equilibrium is achieved.

The linear momentum—that is, mass times speed—of the electron and that of the nucleus of a hydrogen atom (the simplest element) are equal to each other in magnitude but opposite in direction. The electrostatic forces resulting from the attraction of the positively charged nucleus and the negatively charged electron are balanced by the centrifugal forces resulting from the movement of both the spinning electron and the proton. The electron does not revolve precisely around the nucleus (proton), but both revolve about a

point slightly displaced from the proton. The electron, however, is only about 1/1836 the mass of the proton of the hydrogen atom. Thus, to achieve the linear momentum of the proton, the electron must travel about 1836 times faster. Because of this disparity in speeds the nucleus may be considered to be fixed relative to the electron.

The electron moves along a path, called an orbit, about the nucleus somewhat as the planets do about the sun, but the path of the electron need not be rigidly circular or elliptical. Because it must move so rapidly, the electron should not be considered as a point negative charge in space but as a smeared cloud of negative charge surrounding the nucleus. The total elemental atom then consists of a dense central core (protons and neutrons) surrounded by a cloud of negative charge (orbiting electrons), meaning that at any instant much of the atomic volume is unoccupied.

Michel Baranger and Raymond A. Sorensen[13] have made the following comparison: "If an atom were the size of a house, the nucleus would be a pinhead at its center. In actuality atoms are a few hundred-millionths of a centimeter in diameter and on the atomic scale the nucleus seems virtually a point without structure." Yet, as these writers point out, atomic nuclei have size and shape. Two kinds of nuclei exist: "hard," whose shape is permanent, and "soft," whose shape is changeable. Hard nuclei may be spherical or deformed into prolate spheroids (cigar-shaped). Soft nuclei may become oblate, spherical, prolate, and pear-shaped. The soft nuclei oscillate through the different shapes, such as from prolate to spherical, to oblate, back to spherical, then to prolate once again. With time a spherical symmetry is obtained. It is obvious that a simple atom such as hydrogen, with only one proton in its nucleus and one orbiting electron, may be described adequately but most of the elements have atoms with so many protons, neutrons, and electrons that they defy description.

For visualization, the electron orbits may be considered to be circular, although interaction (repulsion) between orbiting electrons perturbs the orbit's form. Figures 2 and 3 show the balance of forces acting on the orbiting electron(s) of the simple hydrogen and helium atoms. Forces similar to those acting on the electron(s) act also on the nucleus.

Certain orbits may be grouped together on the basis of possessing essentially the same energy. A group of such orbits is called a shell. The number of shells will increase to accommodate the number of electrons in the atoms of the elements. Electrons of the lowest energy fill first the shell nearest to the nucleus. These negatively charged electrons are tightly bound by the positive charge on the nucleus. Electrons of slightly greater energy fill the next shell, but these electrons are less tightly held. The populated outer shell of highest energy, called the valence shell, contains the electrons remaining after the lower shells are filled. The electrons in the valence shell possess sufficient

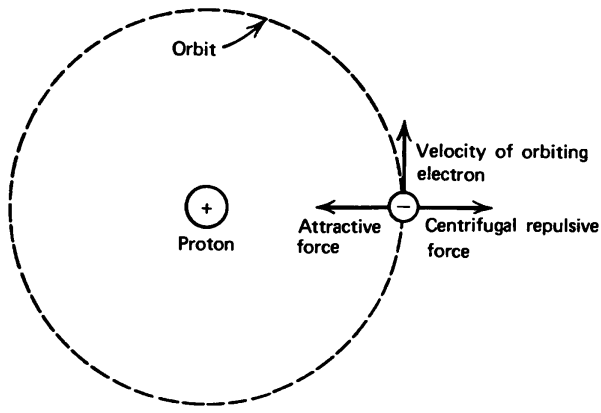

Figure 2. Hydrogen atom with one orbiting electron. [Derived from Sidney W. Benson, *Atoms, Molecules, and Chemical Reactions: Chemistry from a Molecular Point of View*, Addison-Wesley Publishing Company, Reading, Massachusetts, 1970, pp. 38–39.]

energy to interact with other atoms. The valence electrons are only weakly held to the nucleus, and they determine an atom's chemical and spectral behavior.

Seven energy levels or shells are believed to be the maximum number that any one atom may have. These seven shells are designated by the letters K, L, M, N, O, P, and Q, corresponding, respectively, to the principal quantum numbers 1, 2, 3, 4, 5, 6, and 7. (The letters K, L, and M originally designated certain spectral lines resulting from electron transitions observed in X-ray spectra of various elements.) The K shell (1) is nearest the nucleus and can hold only two electrons. The L shell (2) is next and can hold eight electrons. The third or M shell can hold eight electrons, but when there are two electrons in the N shell (4), the M shell can expand to accept 18 electrons. The first five shells of an atom can accept a maximum of 2, 8, 18, 32, and 32 electrons.

Each of the seven principal shells may be subdivided into electronic orbits on the basis of states of orbital angular momentum of the electrons. Each shell may have four subshells, designated s, p, d, and f. (These letters originally designated X-ray spectral lines of visible and ultraviolet radiation: s = sharp, p = principal, d = diffuse, and f = fundamental.) Spectral results indicate that no shell can contain more than two s electrons, six p electrons, 10 d electrons, and 14 f electrons.

Each orbital of a subshell can accept a maximum of two paired electrons. The s sublevel contains only one orbital, accepting two paired electrons of opposite spin. Their opposite spin results in an electromagnetic attraction that couples the two electrons, even though both are negatively charged.

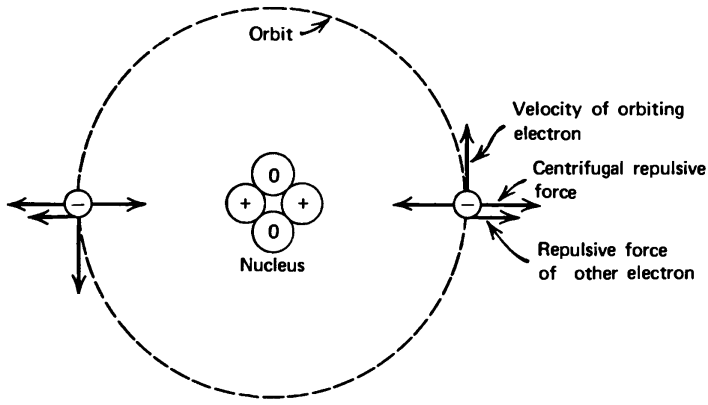

Figure 3. Helium atom with nucleus containing two protons and two neutrons. [Derived from Sidney W. Benson, *Atoms, Molecules, and Chemical Reactions: Chemistry from a Molecular Point of View*, Addison-Wesley Publishing Company, Reading, Massachusetts, 1970, pp. 38–39.]

The *p* sublevel has three orbitals, accommodating a maximum of six electrons of paired spins. The *d* sublevel contains five orbitals with a maximum acceptance of 10 electrons, and the *f* sublevel has seven orbitals with a maximum acceptance of 14 electrons.

The lowest energy electrons of an atom go into the 1*s* orbits of the *K* shell. This orbital is filled by only two electrons. Because the *K* shell of any atom does not possess any more orbitals, it is filled when these two paired electrons are present. The next electrons of lowest energy must go into the 2*s* orbital of the *L* shell. This subshell is also filled with two paired electrons. The next six electrons, if present, will go into the 2*p* orbitals of the *L* shell. Because there are three 2*p* orbitals, one electron will go into each of the three 2*p* orbitals before electron spin pairing occurs. Electrostatic repulsion between electrons causes them to separate spatially. Definite energy and momentum relationships determine how the orbitals of the subshells of the principal shells fill up as the number of electrons increases for each element.[14]

For example, silver has an atomic number of 47, indicating that this element has 47 electrons in orbit about its nucleus. These are distributed as follows:

		Shells									
		K	*L*		*M*			*N*			*O*
		1	2		3			4			5
Atomic	Element	–									–
Number	Symbol	*s*	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*s*
47	Ag	2	2	6	2	6	10	2	6	10	1

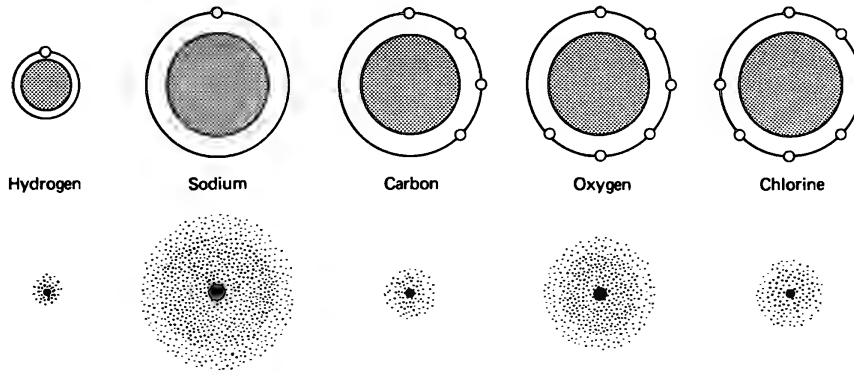

Figure 4. Electrically neutral atoms are depicted schematically across the top. The outer or valence electrons are represented as small circles on the outer circular obit. The dark inner circle is composed of the remaining electrons and the nucleus of the atom. In the more realistic representation at the bottom, each atom is shown as a nucleus (black) surrounded by a cloud of electrons. [Cyril Stanley Smith, *Sci. Am.*, 217(3): 74 (1967)] [Copyright © 1967 by Scientific American, Inc. All rights reserved.]

Actually, the precise state of each electron in an atom is far more complex than has been described so far. But for the purposes of photography such a complex description is not needed. In fact, the chemical reactivity of an atom is largely determined by the electrons in the outermost shell. The electrons in this valence shell are capable of interacting with other atoms. From the viewpoint of photographic chemistry, the atom might be simplified to consist of an inner sphere that includes the nucleus and all the shell electrons except those outer valence electrons that may take part in chemical reactions. A study of these electrons will show how atoms of the elements interact and combine to provide the chemical basis of photography. (See Figure 4.)

Periodic Arrangement of the Elements

The chemical properties of an atom of an element are greatly influenced by its valence electrons. As atomic weight increases, atoms with similar valence shells tend to have similar properties. Elements may be grouped on the basis of valence electrons to give a periodic table of the chemical properties of all the elements.[15] In such a table an element will be situated near other elements of similar properties. Although increasing in atomic weight, elements in vertical columns (families) resemble each other in chemical reactivity. Chemical properties change slowly along horizontal rows of the elements (periods) of such a table. This relationship of families and periods allows scientists to extend the periodic table to predict the properties of elements not yet isolated.

When atoms of an element are widely separated, a state of matter called a gas is formed. Gases diffuse to fill any container they occupy. Hydrogen, helium, nitrogen, oxygen, fluorine, neon, argon, krypton, xenon, and radon are gaseous under ordinary conditions. When the atoms of an element are packed more closely, the element occurs in a liquid state. Liquids flow into a container and assume its form. Under normal temperature and pressure only the elements gallium, bromine, cesium, mercury, and francium are liquids; all of the remaining elements occur as solids. Solids are usually rigid and crystalline in form. Depending on the conditions of temperature and pressure, gaseous elements usually can be changed to liquids, liquid elements to solids, and vice versa.

A family of elements increasing in atomic weight from helium to neon, argon, krypton, xenon, and radon are called the inert gases. These gaseous elements have almost no chemical reactivity. The preparation of the tetrafluoride of xenon in 1962 was considered an astonishing achievement.[16] The outer shell of electrons in each inert gas is completely filled. This filled-shell configuration represents a condition of maximum stability. The atoms of elements other than the inert gases tend either to gain or to lose electrons from their valence shell until an inert-gas configuration (a filled outer shell) is obtained.

Sodium has 11 electrons, one more than the inert gas neon. Sodium tends to lose this one electron, achieving the filled-valence-shell configuration of neon. Sodium now has 11 positively charged protons but only 10 negatively charged electrons. This stable form of sodium, bearing one extra positive charge, is called an ion, or cation since it is attracted to the cathode (−) of an electrolytic cell. The sodium ion, written Na^+ or Na^{1+}, is said to have a valence of one.

Chlorine has two electrons in the 3*s* subshell and five in the 3*p* subshell. Only one more electron is needed to fill all the 3*p* electron orbitals, thus achieving the inert-gas configuration of argon. Chlorine reacts to gain this electron to fill its shell; it then has one more electron than it has protons, resulting in a single negative charge. This chlorine ion, written Cl^- or Cl^{1-}, is called an anion, as it is attracted to the anode (+) of an electrolytic cell.

Valence—the combining capacity of an element—does not indicate the positive or negative character of an ion. Sometimes, however, negative or positive valence values are used to describe ions. Many chemists prefer to use oxidation numbers to describe how compounds are formed from ions. The oxidation number gains one positive unit with each loss of an electron; it gains one negative unit with each electron gained. If an element loses two electrons, the oxidation number is 2+; if it gains two electrons, the oxidation number is 2−.

Both positive and negative oxidation numbers show the ionic charge of the ions. A positive oxidation number represents the combining power of a positively charged ion with a negative ion or ions; a negative oxidation number represents the combining power of a negatively charged ion with a positive ion or ions. A hydrogen ion has an oxidation number of 1+; an oxygen ion, 2−. Two hydrogen ions are needed to combine with one oxygen ion to produce an uncharged molecule of water. Positive and negative ions combine in the smallest number possible to produce an uncharged compound; that is, the positive and negative oxidation numbers of the ions add up to zero.

Elements Exhibiting Variable Valence

Atoms of elements nearer to the center of the horizontal periods of the elements may either gain or lose electrons; thus they can exhibit more than one valence. Actually, about four-fifths of the elements exhibit variable valence. Carbon, for example, has four electrons in its valence shell, which could hold a maximum of eight electrons. If four electrons were gained, the stable complete shell of the element neon would result. But the four electrons could also be given up, resulting in the stable helium configuration. Carbon often reacts as though it were exhibiting oxidation numbers of either 4+ or 4−.

At the beginning of the periodic listing of the elements, the atoms of the elements appear to support the idea that electrons are acquired or given up so as to achieve a filled outer shell (inert-gas configuration). But even among the first 10 elements, beryllium and boron are exceptions. And as the electron structures becomes more populated, the energy of certain of the main levels is essentially the same. In different atoms, sublevels occasionally may interchange. Because of this overlapping of the energy levels, electrons may be added to an underlying shell rather than always to an incomplete outer shell. Thus, valence electrons from two incomplete shells may be involved in interactions with other atoms.

The Bonding of Atoms

Unfilled orbitals in one atom may be filled by electrons from another atom or atoms. The electrons may actually be transferred from one atom to another, resulting in an electrovalent bond of attraction between the two atoms. The mutual sharing of electrons between two atoms, called covalence, can bind the two atoms together. The binding of two or more atoms together produces a molecule. Molecules may be formed by the covalent joining of two like atoms, such as hydrogen, or atoms from different elements, such as hydrogen and chlorine. The molecules resulting from the bonding of different atoms are

often called compounds. The molecule resulting from the bonding of atoms with an electrovalent bond is called an ionic compound, because the ions of unlike charges hold the atoms together.

Besides ionic and covalent bonding, there are three other types of interactions between atoms: metallic, molecular, and hydrogen bonding. In the metallic bond all the atoms of a metallic element share all the valence electrons. Because of the mobility of the electrons between atoms, such elements are excellent conductors of electrical current. The molecular bond is a weak attraction between electrically neutral molecules because of a displacement of positive and negative charge within the molecule. The hydrogen bond is a weak interaction resulting from a charge displacement within the hydrogen atom. The slight positive charge on some hydrogen of one molecule may be attracted by the electronegativity of an atom of another molecule. Generally, materials involve more than one kind of bonding, but the five types of bonding hold together all of the materials of photography.[15] (See Figure 5.)

Some atoms have a tendency to lose one, two, or three of their outer electrons to achieve a completely filled outer shell. These electron-donating atoms, said to be electropositive, become ions with a positive charge equal to the number of electrons lost. The electrons lost are attracted by atoms that seek to fill their orbitals to achieve a filled outer shell. The electron-attracting (electronegative) atoms form ions with a negative charge equal to the number of electrons gained. Although both ions resulting from such an electron transfer may have filled outer shells, the ions are held together by their opposite charges. Ionic compounds are the result.

Silver is an electropositive element, having one 5*s* electron in the O shell of its atoms. Losing this electron would produce a positive silver ion of unit positive charge with filled *s*, *p*, and *d* orbitals of the *N* shell. Chlorine needs only one electron in the third 3*p* orbital to achieve the filled-shell configuration of the inert gas, argon. The chlorine atom is strongly electronegative and will take the electron from a silver atom, forming a positive silver ion and a negative chloride ion. Because of the attraction between these two ions, an ionic compound of silver chloride is produced. This interaction may be represented by using an electron-dot designation that shows as dots only the outer valence electrons of each atom.

$$Ag\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow Ag:\ddot{\underset{\cdot\cdot}{Cl}}:$$

From an electrostatic standpoint the formation of silver chloride might be represented as:

$$Ag^0 + Cl^0 \longrightarrow Ag^+ + Cl^-$$

$$Ag^+ + Cl^- \longrightarrow AgCl$$

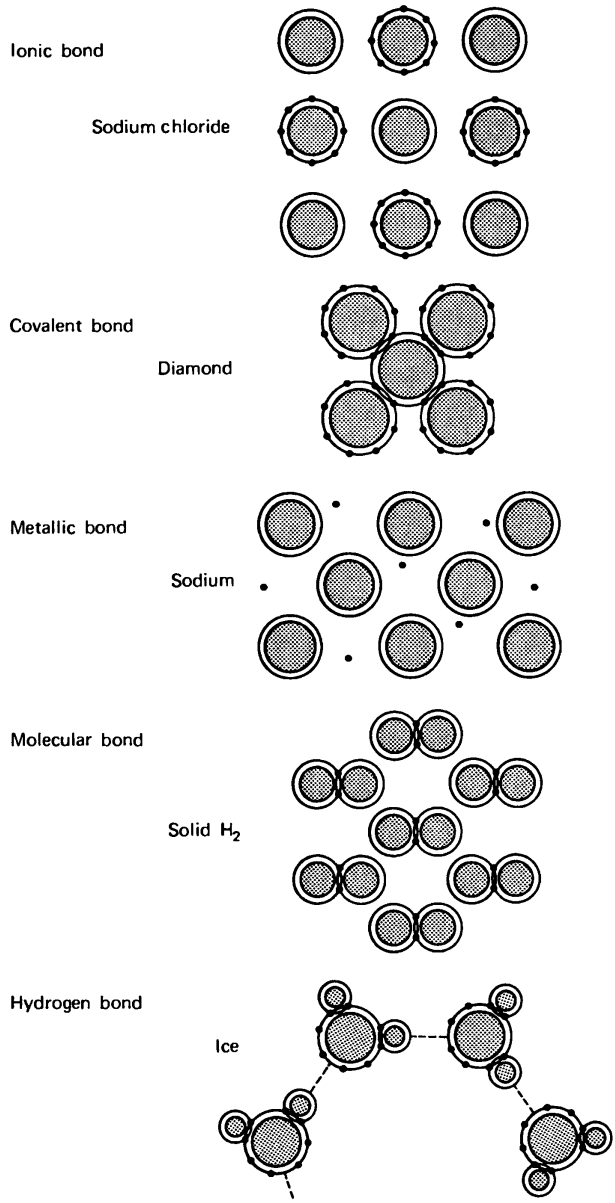

Figure 5. Five types of bonding hold all materials together, as shown here schematically. The ionic bond involves a transfer of electrons but the atoms are held together by charged attraction. The covalent bond results from pairs of atoms sharing their outer electrons. Metallic bonding results when all atoms share all valence electrons. Charge displacement within electrically neutral atoms produces a weak attraction that forms a molecular bond. Charge displacement in the hydrogen atom can also produce a weak attraction exhibited by hydrogen in some of its compounds. Most materials involve more than one type of bonding. [Cyril Stanley Smith, *Sci. Am.*, 217(3): 75 (1967)]
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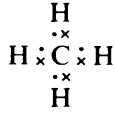
Although the silver chloride is often written as an uncharged molecule (AgCl), it should be remembered that this compound still possesses its ionic character.

Covalent Compounds

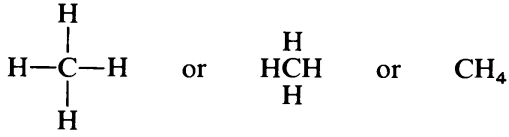
Atoms of elements may combine by the sharing of electrons rather than the ionic attraction resulting from electron transfer. Bonding is considered to result from the overlap of the orbitals of each atom, producing a new orbital that has lower energy requirements than the original atomic orbitals. Both electrons go into the new molecular orbital, which is a cloud surrounding the nuclei of the two atoms.

Carbon has four electrons in its outer shell but does not possess sufficient electron attraction to take four more electrons from other atoms. Carbon atoms, however, do possess a remarkable tendency to share electrons with other carbon atoms or with the atoms of other elements. This tendency has produced the great number of carbon-containing organic compounds that have been isolated or prepared synthetically. One carbon atom with four valence electrons will combine with four atoms of hydrogen (one electron each) to complete the outer shells of each of the five atoms:



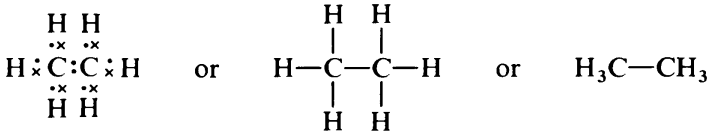
where $\cdot$ = the electron from carbon,
$\times$ = the electron from hydrogen.

For convenient representation this compound is usually written as

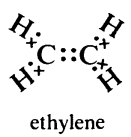


In each case it is assumed that a pair of shared electrons is present between each atom.

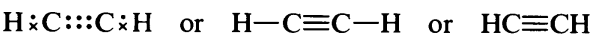
The two-electron covalent bond can occur between carbon atoms, thus making possible long-chain compounds or complex ring structures. Ethane is a simple two-carbon compound exhibiting a covalent bond between the two carbon atoms:



The two carbon atoms have the maximum number of hydrogen atoms needed to form the covalent two-electron bonds. Ethane is said to be a saturated compound. But the carbon-to-carbon bond may also involve four or six shared electrons, called double or triple bonds, respectively. Unsaturated compounds are formed that have less than the maximum number of hydrogens in the molecule. Examples of unsaturated two-carbon compounds are ethylene and acetylene:

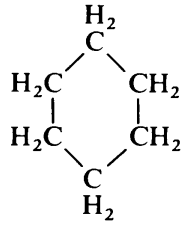


ethylene

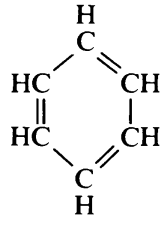


acetylene

Compounds having a carbon ring are also formed by covalent bonding, as shown in the following examples:



cyclohexane



benzene

Cyclohexane is a saturated carbon ring compound in which, as the result of the sharing of electrons, each hydrogen atom has a filled shell of two electrons and each carbon atom has a filled shell of eight electrons. These conditions are also fulfilled in the unsaturated benzene molecule, but the electronic condition in benzene is more dynamic than in cyclohexane. The electrons in benzene flow around the ring in such a fashion as to form many other electronic conditions not indicated by the simple, single notation of benzene as given above. Each bond is equivalent to every other bond. This shifting of electrons around the ring, called resonance, is an important property of compounds that are useful in photographic developing solutions. Resonance makes electrons more readily available for chemical reactions.

The benzene molecule is used so much that special forms of notation have been devised to represent it on paper. Benzene is often written as a hexagon,

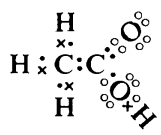
, with the understanding that each angle of the hexagon contains a

carbon atom with a hydrogen atom attached. A more modern notation shows benzene as a hexagon with a closed loop or circle in the center,

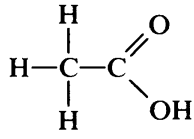
, the loop representing the resonating cloud of electrons. Another form of representation shows the hexagon with dots at each angle,

, each dot being a carbon with sufficient hydrogen atoms attached to satisfy the necessary molecular structure.

Atoms of elements such as oxygen, sulfur, or nitrogen are often present in organic compounds. These atoms may be present in chain or ring compounds. Acetic acid, for example, is a two-carbon compound containing two oxygen atoms:



or

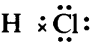


or CH_3COOH

acetic acid

where • = an electron from carbon,
○ = an electron from oxygen,
× = an electron from hydrogen.

The shared pair of electrons between carbon and hydrogen atoms, or between two carbon atoms, are positioned about midway between the two atoms. The reason is that carbon and hydrogen have almost equal electron affinities. But when covalent bonds are formed between atoms of different affinity, the shared electron pair may lie closer to the stronger electron-attracting atom. For example, chlorine is an element whose atoms have a strong attraction for electrons. This attraction is much greater than that of a hydrogen atom. A molecule of hydrogen chloride might be written



with the shared pair of the covalent bond being nearer the chlorine than the hydrogen atom.

The displacement of the covalent electron pair means that the center of negative charge is located nearer the attracting atom and the center of positive charge is nearer the other atom. Such a bond is said to be polar, as there is a charge polarization or charge separation. Such a polar covalent bond, although resembling in some degree an ionic bond, is not its equivalent. Compounds with polar covalent bonds exhibit different properties than do ionic compounds. But the polarization of the electrons in organic and other

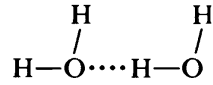
compounds possessing covalent linkages endows these compounds with highly desirable reactivity.

Hydrogen Bonding

Water, the combination of two atoms of hydrogen with one atom of oxygen, is a highly polar compound. This compound might be represented as

where the angle formed by the H to O to H bonds is almost 105 degrees. The oxygen atom attracts all the electrons more strongly than the hydrogen, resulting in the hydrogen's being more positive than the central oxygen atom. Because of this separation of charge, molecules may combine by hydrogen bonding to form aggregates of two or more molecules.

Because of its positive character, the hydrogen in the water molecule is attracted to the more negative atom of another molecule. Two molecules of water may combine to form a dimer:



Hydrogen bonding also occurs within or between identical or different organic molecules that have electronegative atoms that polarize covalent bonds.

ACIDS, BASES, AND SALTS

A number of compounds having certain common properties have been termed acids. Aqueous solutions of these compounds have a sour taste. These solutions will change the blue dye (derived from a lichen) of blue litmus paper to red. Another class of compounds, called bases, have an alkaline reaction when in water solution, converting red litmus paper to blue. Acids and bases react vigorously with one another, so that each loses its acidic or alkaline properties. Acids and bases are said to neutralize each other. The result of the neutralization is water and a compound called a salt.

Many attempts have been made to explain the action of acids and bases. It was noted early that when a gas such as hydrogen chloride was dissolved in water, some of the molecules of hydrogen chloride came apart to form the ions of hydrochloric acid:

$$HCl \longrightarrow H^+ + Cl^-$$

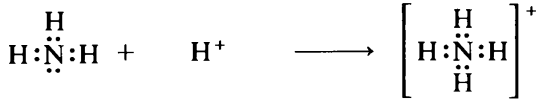
The formation of the ions from the molecule, called dissociation, always produced a positively charged hydrogen ion (a proton) and a negatively charged chloride ion. The water solution of compounds forming H^+ produced an acidic (red) color with litmus paper. An acid was defined as a compound that would produce a proton in water solution.

Sodium hydroxide, a compound of strong alkaline properties, consists of one atom each of sodium, oxygen, and hydrogen. When this compound was dissolved in water, the molecule dissociated into two ions—a sodium ion and an ion consisting of the oxygen and hydrogen that stayed together. This union of hydrogen and oxygen is called a hydroxyl ion.

$$NaOH \longrightarrow Na^+ + OH^-$$

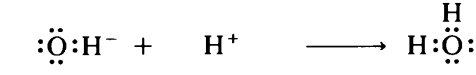
Water solutions of other known alkaline compounds also produced hydroxyl ions in water solution. Such water solutions produced alkaline (blue) color with litmus paper. A base was then considered as a compound that would form hydroxyl ions in water solution.

An acidic compound contains an electron-attracting atom that pulls electrons toward it. This would weaken the bond between this atom and hydrogen, so that a proton (hydrogen minus its electron) would be able to escape easily. This would be a strong acid. Weaker acids would have less electron-attracting power, and the proton would have more difficulty in leaving. The free proton would seek out an electron-rich atom because the proton needs two electrons to complete its shell, such as in the compound ammonia:



ammonia hydrogen ion ammonium ion

or in an ion:



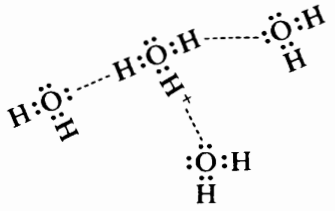
hydroxyl ion hydrogen ion water

The negative charge on the hydroxyl ion also attracts the positively charged proton. Both ammonia and hydroxyl ions are bases, because both accept protons in water solution.

The easy release of protons by a strong acid could be represented by

hydrochloric acid in water hydronium ion chloride ion

The hydronium ion, H_3O^+, indicates that the proton is bound to one molecule of water; that is, the proton is hydrated. Actually, in water solution, the proton may be bound to two molecules of water, $H_5O_2^+$, or three molecules of water, $H_7O_3^+$, or even four molecules of water, $H_9O_4^+$, depending on concentration of hydrogen ions and solution temperature. For simplicity, however, in acid-base reactions, only one molecule of water may be considered, although the hydration of H^+ ions in water should be recognized as the true state.



$H_9O_4^+$

The water molecules act as a base, accepting protons, to form hydronium ions, H_3O^+. The hydronium ion is an acid because it contains an easily released proton. When acids stronger than H_3O^+ are added to water, the acidity of the solution is essentially the same, even though the acids may differ in their release of their protons. This leveling effect of water occurs because the water molecule is a strong enough base to accept all the H^+ released by the strong acids. In each case, no matter how strong the acid is, the hydronium ion, H_3O^+, results. Thus, the strongest acid in water solution is H_3O^+, so that the hydration of the proton brings the acidity level of all strong acids in water solution down to that of H_3O^+.[17]

In Table 3, hydrobromic (HBr), hydrochloric (HCl), hydroiodic (HI), perchloric ($HClO_4$), nitric (HNO_3), and sulfuric (H_2SO_4) acids donate protons so readily that all their protons have been transferred to water. Thus, H_3O^+ is the acid that is present in each case, making the five compounds about equal in acidity in water. Note that some compounds have more than one proton to lose.

When equal molecular quantities of an acid and a base are mixed together in aqueous solution, these compounds lose their distinctive properties, and a new type of compound called a salt is formed. Water is also formed in every case as the result of the reaction between the positive hydrogen ion and the negative hydroxyl ion:

$$H^+Cl^- + Na^+OH^- \longrightarrow Na^+Cl^- + HOH$$

In the above reaction the ions of hydrochloric acid and the ions of sodium hydroxide neutralize each other to form the ions of a salt, sodium chloride

(common table salt), and a molecule of water. Because sodium chloride exists primarily in water solution as the ions, the net result of the neutralization is the formation of a molecule of water.

Proton Acid-Base Theory

According to the proton theory of acids and bases, originated in 1922–1923 by J. N. Bronsted and M. Lowry, an acid is a proton donor—that is, a substance that can readily give up a hydrogen ion. A base is defined as a substance that can accept a proton, as indicated by the relationship:

$$\text{acid} \rightleftharpoons H^+ + \text{base}$$

For the ionization of acetic acid this relationship is written:

$$CH_3COOH \longrightarrow H^+ + CH_3COO^-$$

The proton, however, cannot exist alone in solution. In water solution, the water molecules act as proton acceptors; that is, water acts as a base to form hydronium ions, H_3O^+:

$$\text{base} + H^+ \longrightarrow \text{acid}$$

Hydrogen chloride is a polar covalent compound that will dissolve in water. Chlorine, having a strong electron affinity, holds onto the electron from hydrogen and exists in water solution as a negatively charged ion. The hydrogen ion combines with a molecule of water to form the hydronium ion, H_3O^+:

$$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$$

The tendency of the chlorine to release the proton is very great, so that almost all of the hydrogen chloride is in the form of the ions on the right of the equation. This tendency is shown by the longer arrow pointing to the right.

Sodium hydroxide, an ionic compound, ionizes almost completely in water to give

$$NaOH \longrightarrow Na^+ + OH^-$$

The hydroxyl ion, OH^-, is a strong base; it readily accepts a proton to form a molecule of water. The sodium ion may be replaced by other ions, such as lithium, potassium, and others, and these compounds would be bases because of the presence of the proton-accepting hydroxyl ion.

Table 3. Relative Strengths of Acids in Water

Acid			Conjugate Base	
Name	Formula		Formula	Name
Perchloric	$HClO_4$	↑ *Increasing acidity*	ClO_4^-	Perchlorate ion
Hydroiodic	HI		I^-	Iodide ion
Hydrobromic	HBr		Br^-	Bromide ion
Hydrochloric	HCl		Ci^-	Chloride ion
Nitric	HNO_3		NO_3^-	Nitrate ion
Sulfuric	H_2SO_4		HSO_4^-	Hydrogen sulfate ion
Hydronium ion	H_3O^+		H_2O	Water
Trichloroacetic	CCl_3COOH		CCl_3COO^-	Trichloroacetate ion
Oxalic	HOOC—COOH		$HOOC—COO^-$	Hydrogen oxalate ion
Dichloroacetic	$CHCl_2COOH$		$CHCl_2COO^-$	Dichloroacetate ion
Sulfurous	H_2SO_3		HSO_3^-	Hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-		SO_4^{2-}	Sulfate ion
Phosphoric	H_3PO_4		$H_2PO_4^-$	Dihydrogen phosphate ion
Chloroacetic	$CH_2ClCOOH$		CH_2ClCOO^-	Chloroacetate ion
Hydrofluoric	HF		F^-	Fluoride ion
Nitrous	HNO_2	↓ *Increasing basicity*	NO_2^-	Nitrite ion

Benzoic	C_6H_5COOH	↑	$C_6H_5COO^-$	Benzoate ion
Hydrogen oxalate ion	$HOOC—COO^-$		$^-OOC—COO^-$	Oxalate ion
Acetic	CH_3COOH		CH_3COO^-	Acetate ion
Propionic	CH_3CH_2COOH		$CH_3CH_2COO^-$	Propionate ion
Carbonic	H_2CO_3		HCO_3^-	Hydrogen carbonate ion
Hydrogen sulfide	H_2S		HS^-	Hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$		HPO_4^{2-}	Monohydrogen phosphate ion
Hydrogen sulfite ion	HSO_3^-		SO_3^{2-}	Sulfite ion
Hypochlorous	$HClO$		ClO^-	Hypochlorite ion
Hydrogen cyanide	HCN		CN^-	Cyanide ion
Ammonium ion	NH_4^+		NH_3	Ammonia
Boric	H_3BO_3		$H_2BO_3^-$	Dihydrogen borate ion
Hydrogen carbonate ion	HCO_3^-		CO_3^{2-}	Carbonate ion
Monohydrogen phosphate ion	HPO_4^{2-}		PO_4^{3-}	Phosphate ion
Hydrogen sulfide ion	HS^-		S^{2-}	Sulfide ion
Water	H_2O		OH^-	Hydroxyl ion
Hydroxyl ion	OH^-		O^{2-}	Oxide ion
Ammonia	NH_3	↓	NH_2^-	Amide ion

Increasing acidity ↑ ↓ *Increasing basicity*

Source: Gerard A. Kass, *Individual Study Program in Chemistry*. Vol. V. *Acid-Base Chemistry*, Addison-Wesley Publishing Company, Inc., 1969.

When a strong acid reacts with a strong base, neutralization is said to have occurred. The acidic and basic properties of the reactants are destroyed, and a salt and water are formed. The reaction of sodium hydroxide with hydrochloric acid may be written:

$$H_3O^+ + Cl^- + Na^+ + OH^- \longrightarrow 2H_2O + Na^+ + Cl^-$$

In water solution the Na^+ and the Cl^- remain as ions, having played no part in the neutralization reaction. Neutralization, then, may be written:

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

Water has been formed, and water is neither acidic or basic; that is, water is neutral. When the water is removed, the salt, sodium chloride, can be isolated as a solid having a crystal structure that is held together by the attraction of the oppositely charged ions.

When NaCl is dissolved in water, the compound forms Na^+ and Cl^-, but neither ion reacts with water to any extent. The solution is neither acid or basic. Some salts, however, do react with water and form solutions that are acidic or basic. The splitting of the water molecule, called hydrolysis, is the reverse of neutralization, during which water is formed. For example, sodium carbonate, Na_2CO_3, produces Na^+ and CO_3^{2-} in water. Sodium ions do not interact appreciably with water molecules. The carbonate ion, however, is a strong base—that is, a proton acceptor.

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$$

Hydrolysis produces hydroxide ions, and the solution is basic.

Other salts produce acidic solutions. When aluminum chloride is dissolved in water, the trivalent aluminum ion hydrates, taking up six molecules of water:

$$Al^{3+} + 6H_2O \longrightarrow Al(H_2O)_6^{3+}$$

The hydrated aluminum ion can then act as a proton donor; that is, it is an acid.

$$Al(H_2O)_6^{3+} \longrightarrow [Al(H_2O)_5OH]^{2+} + H^+$$

Hydronium ions, H_3O^+, result from dissolving aluminum chloride in water. The chloride ion does not remove an appreciable number of protons from water, so the solution is acidic from the presence of the hydrogen ions that result from the interaction of hydrated aluminum ions with water molecules.

The Lewis Acid-Base Theory

It was soon realized that the proton theory of acids and bases, while true and very useful, was inadequate to explain the acidic and basic properties of

substances that did not release protons or hydroxyl ions. Compounds also appeared to be acting as acids or bases in solvents other than water. To explain acid-base reactions under a wider range of conditions, Gilbert N. Lewis formulated the electronic theory of acids and bases.[18,19] The Lewis theory incorporates the proton theory but as a specific case of a broader concept.

A Lewis acid was defined as a substance that could accept a pair of electrons from a donor, the Lewis base. The reaction of an acid with a base results in the formation of a covalent bond in which both shared electrons are provided by the base. Such a bond has sometimes been called a coordinate covalent bond. The presence of protons, hydroxyl ions, or water is not required, although the Lewis concept embraces them as well.

$$\text{Acid} + \text{base} \longrightarrow \text{covalent compound}$$

$$H_3O^+ + :\ddot{O}:H^- \longrightarrow 2H:\ddot{O}:H$$

$$Cl:\ddot{B}(:Cl:) + :\ddot{N}:H \longrightarrow Cl:\ddot{B}(:Cl:)\,:\ddot{N}:H$$

The reaction of a hydronium ion with a hydroxyl ion to form water is essentially the same result as provided by the proton theory. But the donation of an electron pair by ammonia to boron trichloride to form a covalent link does not involve proton transfer. The boron trichloride is the acid accepting an electron pair, even though it contains no hydrogen at all. And the ammonia is the base donating an electron pair, although it does contain OH^-.

The Measure of Acidity of an Aqueous Solution

The water molecule, consisting of a hydrogen ion and a hydroxyl ion, may act either as an acid or a base. The interaction of two water molecules may be written:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Most water exists as un-ionized molecules, as indicated by the longer arrow pointing to the left. The number or concentration of the acid (H_3O^+ or, more simply, H^+) and base (OH^-) ions is equal. Water is neither acidic nor basic but neutral.

In 1909, S. P. Sorenson originated the symbol pH (pronounce each letter: pee aitch) to express the hydrogen ion concentration in an aqueous solution, defining

$$\text{pH} = \log_{10} \frac{1}{\text{concentration of } H^+ \text{ in moles per liter}}$$

The equation states that the pH is equal to the logarithm (base 10) of the reciprocal of the concentration of the hydrogen ions in moles per liter of aqueous solution. In water there are 0.0000001 mole of hydrogen ions per liter and 0.0000001 mole of hydroxyl ions per liter at 25°C. At this temperature the pH of water is

$$\text{pH} = \log_{10} \frac{1}{0.0000001} = -\log_{10} 10^{-7} = 7$$

Any water solution having a number of hydrogen ions equal to that of pure water is said to have a pH of 7.

Increasing the number of hydrogen ions in solution will result in a decrease in an identical number of hydroxyl ions, as the product of the concentrations of the two ions is a constant. In pure water the concentration of the hydroxyl ions is equal to the concentration of the hydrogen ions. The pH = 7 but also pOH = 7, using the same convention as used to determine the pH, and pH + pOH = 14. The pOH might be used as a measure of alkalinity, but in practice pH is used for both acid and alkaline solutions.

Acidity increases (alkalinity decreases) by a factor of 10 for each pH unit less than 7, the value of neutrality. A solution of pH 5 is 10 times as acid as a

Table 4. The pH and pOH Scales

Hydrogen Ions (moles per liter)		pH Scale			pOH Scale			Hydroxyl Ions (moles per liter)
1.0	or	10^{-0}	0	*Highly acid*	14	10^{-14}	or	0.00000000000001
0.1		10^{-1}	1	↑	13	10^{-13}		0.0000000000001
0.01		10^{-2}	2	↑	12	10^{-12}		0.000000000001
0.001		10^{-3}	3	↑	11	10^{-11}		0.00000000001
0.0001		10^{-4}	4	↑	10	10^{-10}		0.0000000001
0.00001		10^{-5}	5	↑	9	10^{-9}		0.000000001
0.000001		10^{-6}	6	↑	8	10^{-8}		0.00000001
0.0000001		10^{-7}	7	*Neutral*	7	10^{-7}		0.0000001
0.00000001		10^{-8}	8	↓	6	10^{-6}		0.000001
0.000000001		10^{-9}	9	↓	5	10^{-5}		0.00001
0.0000000001		10^{-10}	10	↓	4	10^{-4}		0.0001
0.00000000001		10^{-11}	11	↓	3	10^{-3}		0.001
0.000000000001		10^{-12}	12	↓	2	10^{-2}		0.01
0.0000000000001		10^{-13}	13	↓	1	10^{-1}		0.1
0.00000000000001		10^{-14}	14	*Highly alkaline*	0	10^{-0}		1.0

solution of pH 6 and 100 times as acid as a solution of pH 7. Alkalinity increases (acidity decreases) by a factor of 10 for each pH unit more than 7. A solution of pH 10 is only 1/10 as acid as a solution of pH 9, and only 1/100 as acid as a solution of pH 8. Any two-unit change represents a 100-fold change, a three-unit change a 1000-fold change in ionic concentration.

The Measure of Silver Ion Concentration

In some photographic operations silver ion concentration must be determined, and this quantity is expressed as pAg (say "pee a gee" without pause).

$$\text{pAg} = \log_{10} \frac{1}{[\text{Ag}^+]}$$

At the point of neutrality the silver ion concentration $[\text{Ag}^+]$ equals the halide ion concentration $[\text{halide}^-]$. Below this value, at low pAg values, there is an excess of silver ions; above this value there will be an excess of halide ions (high values of pAg but low concentrations of silver ions).[20]

The numerical values of pH and pAg are often obtained by direct measurement of an electrochemical cell, such as with a pH meter. For practical pH measurements, such a cell usually consists of a glass electrode and a reference electrode (a normal calomel electrode, for example). The pAg measurements may use the same reference electrode with a metallic silver electrode. With either pH or pAg measurements, the value of the potential of the cell is determined by a voltmeter that is calibrated to read in pH or pAg numbers.

The acidity or alkalinity of an aqueous solution may be estimated by using dyes that change color with pH. Litmus is an indicator dye that is red in solutions of pH less than 6.5, but blue above pH 7.5. As the dye molecule ionizes, the color changes from red to blue. Many other dyes are available that have distinctive acid and base colors. One or more of these dyes may be impregnated into narrow paper strips that are sold as indicator papers. Spotting a drop of a photographic solution on the indicator paper will produce a color that may be compared with a standard set of colors calibrated in pH units.

CARBON COMPOUNDS

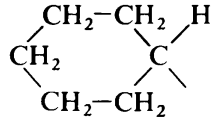
Elements combine either with themselves or with other elements to form compounds. The vast majority of these compounds contain carbon; in fact, more than a million carbon-containing compounds are known. Carbon is unique in its power of combining to form stable atomic structures. An atom of carbon contains four electrons in its valence shell, the *L* shell, and carbon

may either lose four electrons or gain four electrons to reach the nearest inert gas configuration.

Losing one electron would make the carbon atom become positively charged. The losing of a second electron would be more difficult, because the positive charge would increase the binding power of the atom for its electrons. Losing a third or fourth electron would even be less possible. On the other hand, gaining one electron would cause the carbon atom to become negatively charged. Gaining a second negatively charged electron would be more difficult because of the repulsion of like charges. Gaining a third or fourth electron would require considerable energy. Carbon has resolved its electronic difficulty by usually sharing its electrons with other atoms of carbon or other elements. In this way, carbon completes the eight electrons needed for its *L* shell, forming very stable compounds of great diversity. Some of these compounds are essential for making and processing photographic materials.

Some carbon compounds involve four two-electron bonds to each carbon. The two-electron bonds may be formed between carbon atoms or between carbon and another element, such as hydrogen. In such carbon-hydrogen compounds (hydrocarbons) only two-electron bonding occurs between carbon-carbon or carbon-hydrogen, and the compound is said to be saturated (maximum number of hydrogens). When carbon forms double (four-electron) or triple (six-electron) bonds with other carbon atoms, less than the maximum number of hydrogens is present, and the compound is said to be unsaturated.

Carbon-and-hydrogen compounds are relatively unreactive, but in the form of groups they are often used to make other, more reactive molecules. Such groups may be in the form of straight chains (CH_3—, methyl; CH_3CH_2—, ethyl; $CH_3CH_2CH_2$—, propyl; or $CH_3CH_2CH_2CH_2$—, butyl), branched chains (such as the tertiary- or iso-butyl group, $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—CH_3$), or rings such as phenyl, , or hexyl,



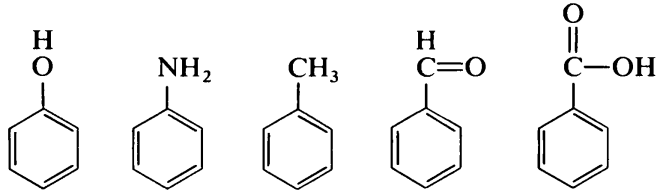
The characteristics of organic molecules that have important photographic properties, however, are largely determined by substituents attached to the carbon-hydrogen compound. These substituents, called functional groups, usually contain elements of greater electronic reactivity than carbon and

hydrogen. Similar reactivity may be conferred upon different atomic structures bearing the same substituent group. Thus, a group of related carbon structures containing an $—NH_2$, an amino functional group, would tend to have somewhat similar properties because of the $—NH_2$ that is common to the compounds.

The name of the functional group is often used as a prefix with compound class names. Thus, nitrobenzene has an $—NO_2$ attached to the benzene ring, or bromohydroquinone has a —Br attached to the ring of hydroquinone. All compounds containing the same functional group are classed by the same name. For example, all compounds containing an $—NH_2$ group are amines in general. The principal functional groups are listed in Table 5. In this listing the straight line or lines attached to the functional group structure are two-electron bonds, usually to carbon atoms. In the case of some simple compounds, such as amide, aldehyde, and carboxylic acid, a hydrogen atom may be sufficient.

Benzene is the parent compound of a large class called aromatic compounds. Because of the nature of its oscillating electrons, it is difficult to depict on paper. This electronic condition is sometimes shown as:

If benzene is written with the double bonds in one configuration, the other depiction of the bond location is equally acceptable, as this method is only a convenience of illustration and not a true representation of the electronic condition of the molecule. Benzene derivatives are often named by using common names that include the presence of the functional group. Some of these more important common benzene derivatives include:



phenol aniline toluene benzaldehyde benzoic acid

Substituents on the benzene ring are usually located by the number of the carbon atoms to which the substituents are attached. The benzene ring is numbered in a clockwise manner:

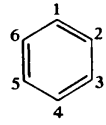
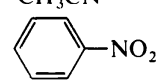
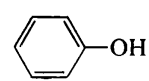


Table 5. Principal Functional Groups of Organic Compounds

Name of Functional Group	Structure of Group	Class of Compounds Containing Group	Typical Example of Compound: Structure	Typical Example of Compound: Name
Amino	$-NH_2$	Amine (primary)	$CH_3CH_2-NH_2$	Ethylamine
	$>NH$	Amine (secondary)	$(CH_3CH_2)_2NH$	Diethylamine
	$>N$	Amine (tertiary)	$(CH_3CH_2)_3N$	Triethylamine
Cyano or nitrilo	$-C\equiv N$	Nitrile or cyanide	CH_3CN	Acetonitrile
Nitro	$-NO_2$	Nitro compound		Nitrobenzene
Hydroxy	$-OH$	Phenol (benzene derivative)		Phenol (hydroxybenzene)
Hydroxyl	$-OH$	Alcohol (primary) (chain compound)	CH_3CH_2OH	Ethyl alcohol (ethanol)
		Alcohol (secondary)	$CH_3CH(OH)CH_3$	Isopropyl alcohol

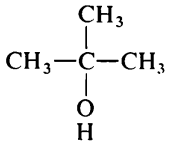
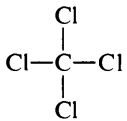
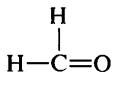
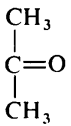
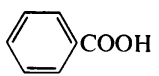
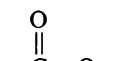
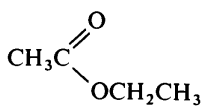
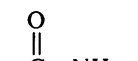
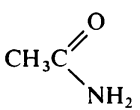
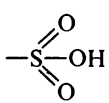
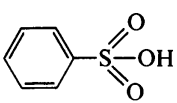
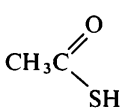
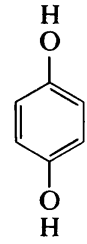
		Alcohol (tertiary)		Tertiary-butyl alcohol (*t*-butyl alcohol)
Ether	—O—	Ether	$CH_3—O—CH_2CH_3$	Methyl ethyl ether
Bromo- (or Chloro-, or Fluoro-, or Iodo-)	—Br (—Cl, —F, or —I)	Halide		Carbon tetrachloride
Carbonyl		Aldehyde		Formaldehyde
Carbonyl		Ketone		Acetone
Carboxyl		Carboxylic acid	$HCOOH$	Formic acid
			CH_3COOH	Acetic acid
			CH_3CH_2COOH	Propionic acid
				Oxalic acid
				Benzoic acid

Table 5. (*continued*)

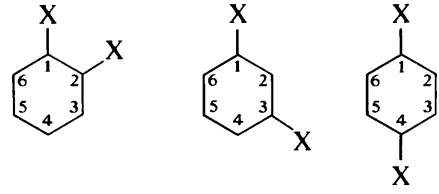
Name of Functional Group	Structure of Group	Class of Compounds Containing Group	Typical Example of Compound	
			Structure	Name
Carboxy		Carboxylic acid ester		Ethyl acetate
Amido		Amide		Acetamide
Sulfo; sulpho		Sulfonic acid, sulphonic acid		Benzene sulfonic acid
Mercapto	—SH	Mercaptan	CH_3CH_2SH	Ethyl mercaptan
		Mercapto carboxylic acid	$HSCH_2COOH$	Mercapto acetic acid
Thio	—SH	Thio acid		Thioacetic acid

Thus, in the compound



the two substituents are located on the 1 and 4 carbon atoms. One possible name would be 1,4-dihydroxybenzene. Because the compound is a phenol, the compound may be named as 4-hydroxyphenol, the —OH of the phenol being in the 1 position.

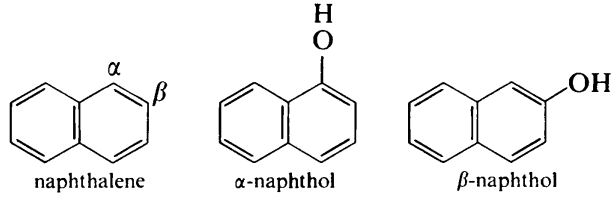
There is another naming system for locating two substituents on the benzene ring. If the two substituents are on adjacent carbon atoms (the 1 and 2 positions), the two groups are said to be ortho to each other. If one ring carbon separates the two constituents, the configuration is called meta (1 and 3 positions occupied); if two carbons separate the two constitutents, the groups are said to be para to each other (located in the 1 and 4 positions). These structural configurations are shown below.



ortho abbreviated as *o-* | meta *m-* | para *p-*

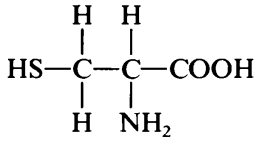
The compound, 1,4-dihydroxybenzene, may also be called paradihydroxybenzene, usually written *p*-dihydroxybenzene. This compound also has a common name—hydroquinone—and is an important developing agent.

The order of the letters in the Greek alphabet [(1) alpha (α), (2) beta (β), (3) gamma (γ), (4) delta (δ), and so on] has been used to locate substituents in carbon compounds. This method is often used with the naphthols:



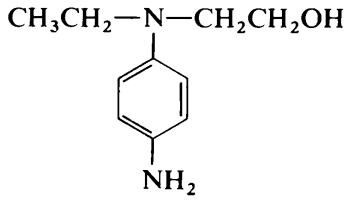
naphthalene | α-naphthol | β-naphthol

In carboxylic acids the carboxyl group is not given a Greek letter, but the lettering begins with the first carbon attached to the carboxyl and continues on the carbon chain. Thus, the compound, 2-amino-3-mercaptopropionic acid,



could be called α-amino-β-mercaptopropionic acid, although cysteine is its common name.

Greek letters are often used to designate groups in alkyl substitutions, as shown in the following case:



N-ethyl-*N*-(β-hydroxyethyl)-*p*-phenylenediamine

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Chapter 2
The Photographic Material

The art of preparing highly sensitive photographic emulsions can be regarded essentially as the art of introducing certain impurities into the silver halide in a particular way.

A. P. H. TRIVELLI[391]

In an instant a photographic film is exposed. Light is imaged on the sensitive layer of the photographic film, but no change is visible in the gelatin suspension of the fine crystals of the silver salts. Certain atomic events, however, have taken place that make photography possible. Slowly, the mystery of the unseen or latent image is being revealed. A knowledge of the composition of photographic materials, and the best conception of how the latent image is formed, are prerequisites to understanding the modern concepts of photographic processing.

THE PHOTOGRAPHIC MATERIAL

The Silver Salts

The photographic layer is a dispersion of light-sensitive solid particles, really microcrystals but often called grains, in a water-permeable medium that can be adhered to a suitable base material. Many compounds are

affected by light, but so far only the salts of silver have shown the high sensitivity necessary for photography. The most light-sensitive of the salts of silver involve a family of elements called the halogens. Because they were found in sea salt, these elements were named after the Greek word for the salt sea.[1]

The halogens are fluorine, chlorine, bromine, and iodine, with their atomic mass increasing in that order. They combine with silver in a one-to-one ratio to produce the salts called the silver halides. The halides most useful in photographic materials are silver chloride, silver bromide, and silver iodide; silver fluoride is not particularly valuable here.

A silver halide grain in a photographic layer is extremely small, ranging from a fraction of a micron for a high-resolution film to slightly more than one micron for an X-ray film. (A micron is 39 millionths of one inch or one thousandth of one millimeter.) Most black-and-white or color films contain primarily silver bromide with a very small amount of silver iodide. Slower films and papers of higher contrast may be made with silver chloride, or silver bromide, or a combination of both. In certain photographic products all three of these silver halides may be present. In the mixed silver halide products the chloride may be present in concentrations up to that of the bromide. Iodide, however, rarely exceeds 10% of the total halide content. Higher iodide concentrations do not give increased light sensitivity, and they may interfere with the processing of the exposed photographic material.

In a silver bromide microcrystal in the photographic layer, commonly referred to as the emulsion layer, the silver and the bromide alternate, first a silver, then a bromide, another silver, another bromide, and so on, row beside row, layer atop layer, until many millions of atoms of these two elements are present in a three-dimensional lattice arrangement. This crystal structure is held together by the attraction of the positively charged silver for the negatively charged bromide. Such charged atoms, either positive or negative, are called ions. The microcrystal or grain of silver bromide in a photographic emulsion is thus composed of an ordered structure of silver ions and bromide ions.

Ag^+ Br^- Ag^+ Br^- Ag^+ Br^- Ag^+

Br^- Ag^+ Br^- Ag^+ Br^- Ag^+ Br^-

Ag^+ Br^- Ag^+ Br^- Ag^+ Br^- Ag^+

Br^- Ag^+ Br^- Ag^+ Br^- Ag^+ Br^-

Ag^+ Br^- Ag^+ Br^- Ag^+ Br^- Ag^+

a single plane of a silver bromide crystal

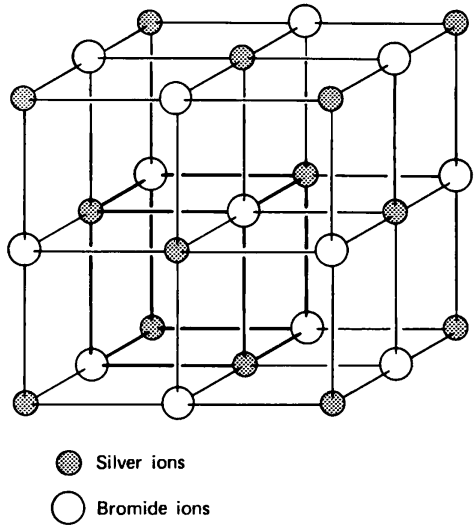


Figure 1. Parallel planes of the AgBr crystal showing the cubic lattice. The individual unit is a cube containing four silver and four bromide ions at the corners.

The smallest individual unit in the structure is a cube with the silver and bromide ions at the opposite corners, each cube having four silver and four bromide ions. (See Figure 1.) This unit is repeated many times in each individual grain. One face of the cube serves as one face of the adjoining cube. This type of ionic structure is called a cubic crystal lattice. Silver chloride and silver bromide have crystal structures of this type, but not silver iodide. However, silver iodide crystals are usually not used in emulsions, but the iodide is incorporated into the crystals of the chloride or the bromide. In grains containing more than one halide, the chloride and the bromide are in the same cubic lattice structure, mixing freely in all proportions throughout the crystal but at random. The presence of bromide ions in a silver chloride crystal lattice does cause some strain, however. Considerable deformation and expansion are produced when iodide ions are present in silver chloride or silver bromide crystals. About 32% iodide can be incorporated in the crystals before silver iodide crystals are formed separately; such high percentages of iodide are not used in photographic materials.[2] The small amount of iodide may be concentrated at the center of the grain, or near the surface, or otherwise localized, depending upon the method used to prepare the emulsion.[3–4]

Silver bromide or silver chloride microcrystals in the photographic emulsion have cubic lattices, but the crystals may be of different shapes. (See Figure 2.) The exact form is determined by the concentration of the

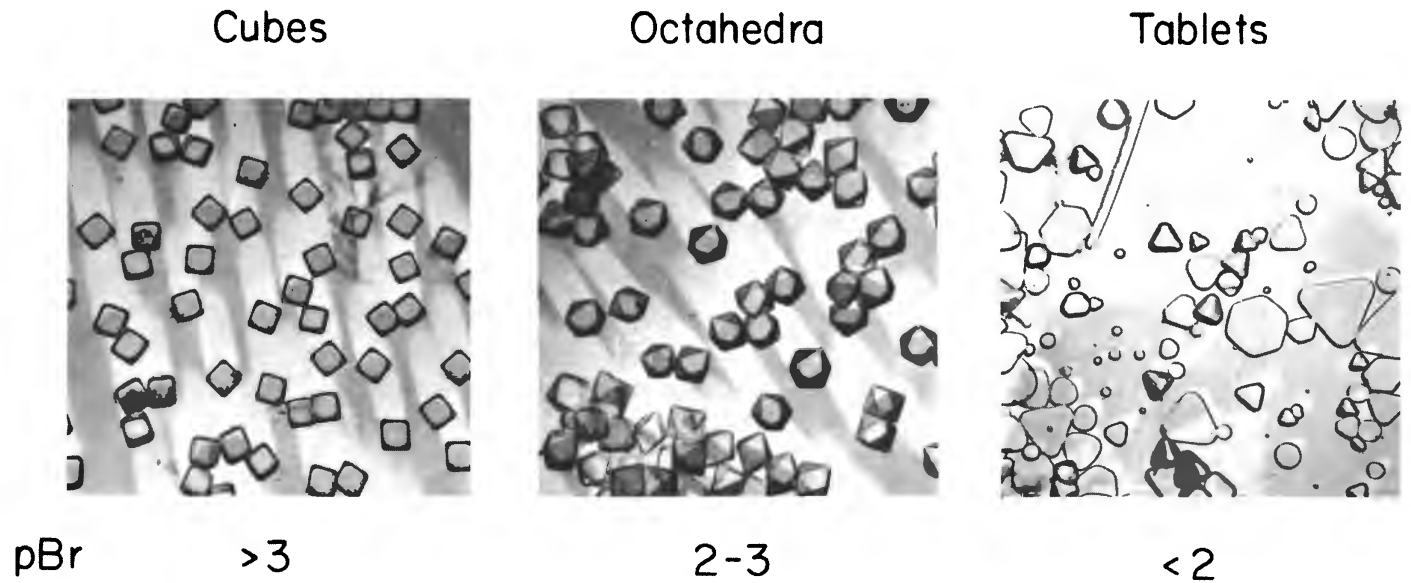


Figure 2. Electron micrographs (preshadowed carbon replicas) showing the form of silver bromide crystals obtained from double-jet precipitation in bone gelatin at the indicated bromide concentration. [C. R. Berry, S. J. Marino, and C. F. Oster, Jr., *Photo. Sci. and Eng.*, 5: 332 (1961)]

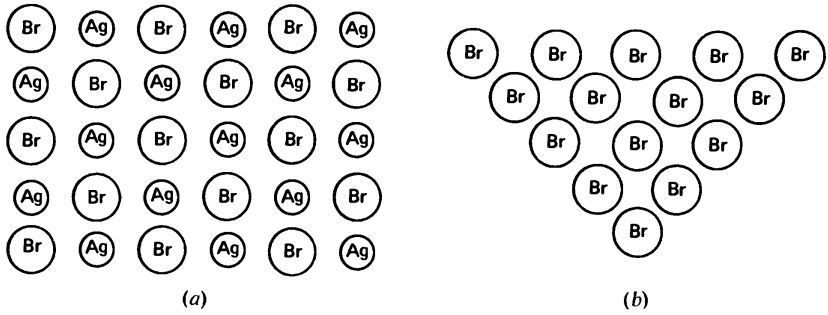


Figure 3. Ions in crystal faces. (*a*) Cubic face. (*b*) Octahedral face.

excess ions during emulsion making, the concentration of silver halide solvents also present, and the properties of the colloidal vehicle, such as gelatin, present during the precipitation of the microcrystals.[5–6] Compounds that cause the crystals to be retarded from growth along certain planes of the crystal can produce cubes, spheres, or octahedra. Needles, pyramids, flat platelets, or triangular grains may be formed during precipitation. Excess potassium bromide produces a considerable number of tabular silver bromide microcrystals.[7] If there is no excess of potassium bromide, almost perfect cubes can be produced. The faces of cubic crystals have alternating silver and bromide ions, but octahedral faces are either all silver ions or all bromide ions.[8–9] (See Figure 3.)

About one million ion pairs have been estimated to be in the smallest silver halide grains and about five thousand times that many in the largest grains. Because of this great number of ions, it is almost a certainty that perfect cubic lattices will not be formed. A variety of irregularities are built into each grain during the rapid formation of the crystal. About 4% iodide produces crystal twinning and dislocations. Some imperfections are the result of missing or misplaced ions. One row of ions may be mismatched with a nearby row of ions. The crystal may be incompletely formed and its faces terraced. Other defects and dislocations may result from the lack of crystal perfection.[10,11] Some of the irregularities play an essential part in the formation of the latent image, particularly in internal image formation. The role of crystal irregularities in latent image formation will be discussed in the next chapter.

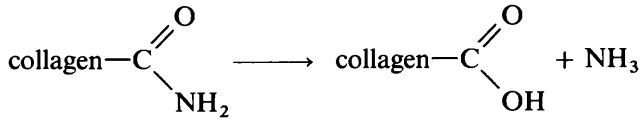
The Gelatin

When R. L. Maddox in 1871 decided to disperse his silver salts in gelatin, he was seeking a better way to make a photographic emulsion layer for

glass plates.[12] Gelatin had been used by others—by Robert Bingham[13] in 1850, William H. Harrison[14] in 1868, and probably even by William Henry Fox Talbot as early as 1836—but the account by Maddox in 1871 stimulated others to make gelatin dry plates.[15–18] Before that time, the light-sensitive plate had to be prepared, then exposed and developed while still wet. The use of gelatin allowed photographic materials to be made far in advance of actual use, and, after exposure, processing could be delayed until convenient. Unknown to Maddox, however, the choice of gelatin was most fortuitous. Without gelatin today's high-speed photographic films could not exist. And even after almost 100 years of the preparation of gelatin–silver halide photographic products, much is yet to be learned about this complex and reactive material that seems to influence everything it contacts.

Gelatin does not occur in nature. It is a commercial product derived from the principal protein of the skin, bones, and sinew of animals.[19] This fibrous protein—collagen—is believed to consist of three chains, each a helical coil, wound tightly around themselves to produce a triple helix structure.[20] In some collagens the chains may also be linked together, possibly by sugarlike molecules.[21–22] Although the nature of the tightly wound chains is not completely known, the structure of the collagens is being revealed by modern analytical techniques.

Gelatin is derived primarily from the collagen contained in animal bones or hides, such as pigskins or calfskins; other sources are animal connective tissue and sinew. The production of bone gelatin requires that the inorganic content of the bones be removed first. This is accomplished by a few days' treatment in dilute hydrochloric acid. The insoluble tricalcium phosphate, $Ca_3(PO_4)_2$, is converted to the soluble monocalcium salt, $CaH_4(PO_4)_2$, during the acid demineralization leaching treatment.[23] Dimineralized bone, called ossein, is then washed and treated with dilute alkali (lime or sodium hydroxide) to neutralize any residual acid. The neutralized ossein is soaked in a suspension of hydrated line for 60 to 100 days.[24] During this period many of the carboxyl groups of the collagen are freed from their original acid amide form:

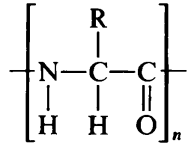


Gelatin derived from alkali-processed collagen contains more acidic than basic groups in the molecule and thus exhibits its point of least solubility in acidic solution. During liming and subsequent treatment, the helical structure of the collagen is broken up, producing long, coiled chains of the substance called gelatin.

Gelatin is extracted from the limed ossein, after washing and neutralization and washing again, by the use of hot water, starting at about 50°C and gradually increasing the temperature to boiling. Each extract is filtered, deionized, and concentrated before chilling and drying. The nature of the long acid and alkali treatments, followed by the thermal extraction, has a great influence upon the character of the gelatin obtained. For example, the harsh liming treatment may be replaced by a dilute acid treatment of dehaired animal skins, such as pigskins, for only a short time.[25–26] Only a warm-water extraction is used to isolate the gelatin. This milder treatment of the collagen produces a gelatin that exhibits its minimum point of solubility in alkaline solution rather than on the acid side as with lime-treated collagen. This gelatin has more of its carboxyl groups tied up in the acid amide form. It may contain more impurities than the lime-treated gelatin derived from bones and hides. Most of the gelatin now used in photographic materials is of the type obtained from the harsher lime treatment, but modern deionizing techniques can make acid-treated gelatin suitable.

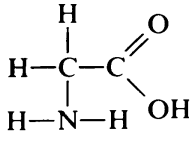
Gelatin is the result of the cleaving of the three molecules that are wound around each other in ropelike fashion in the triple helix of the crystalline regions of collagen. In the noncrystalline regions the single strands are unordered but have crosslinks between their functional groups. Photographic gelatin contains these molecules as single chains, a thermoplastic polymer whose exact structure depends upon the collagen and the various treatments needed to extract the gelatin chains from the crosslinked bonding of the crystalline and noncrystalline portions of the collagen. Each long-chain gelatin molecule is composed of α-amino and imino acids joined together by

—C—N— linkages called peptide bonds. The general formula of the polypeptide molecule of gelatin is, according to J. E. Jolley,[27] "deceptively simple":

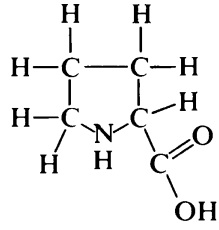


where n represents from 500 to 1000 amino acid units or residues. The R represents a side chain of the amino acid that contains functional groups that make gelatin soluble in water. Jolley states: "In aqueous solution, the gelatin molecules exist as single chains in random configurations, sheathed by water molecules. The random structure persists under conditions of hot drying, e.g., at 50°C, but partial crystallization (i.e., gelation) occurs on 'cold' drying, e.g., at 10°C."

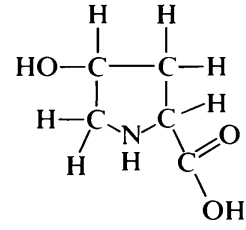
There are 18 amino acids in the polypeptide chain of gelatin.[28–29] (See Table 1.) Their sequence in the chain is not known completely. Fifty-eight percent by weight of gelatin is composed of three amino acids:



glycine (27.5%)

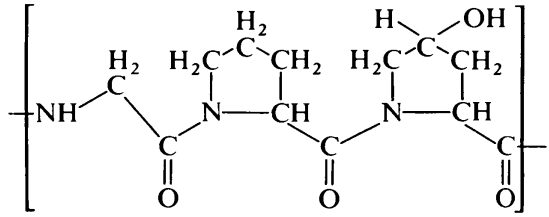


proline (16.4%)



hydroxyproline (14.1%)

Glycine, therefore, constitutes almost one-third of the amino acids in gelatin, and proline and hydroxyproline constitute almost another third. In the gelatin molecule glycine is usually present at every third place for an amino acid along the polypeptide chain.[30] The other amino acids fill in the other two sites, but one preferred sequence is

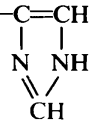


—glycine—proline—hydroxyproline—

The repeated sequence of three amino acids has been shown to be able to form chains that intertwine to form the triple-stranded helix of collagen, the chains possibly being bonded together by the hydrogen on the amino group of glycine to the $-\overset{\overset{O}{\|}}{C}-$ of a proline on one of the other gelatin chains.

Many of the other one-third of the amino acids of gelatin are present as side chains that have terminal amino or carboxylic acid groups.[31] Arginine and lysine, for example, have terminal amino groups, and aspartic acid and glutamic acid have terminal carboxylic acid groups. Hydroxy groups, such as on hydroxyproline or serine, are also present in the gelatin chain. Amino, hydroxy, and carboxylic acid groups account for most of the water solubility of gelatin. Gelatin can act as either an acid or a base, because the gelatin molecule contains both the basic amino groups and the acidic carboxylic acid groups; that is, the molecule has amphoteric properties. Except at high acidity or high alkalinity, both $-\overset{+}{N}H_3$ and $-COO^-$ are present in the

Table 1. Amino Acid Composition of Gelatin and Collagen

Amino Acids $H_2N—CHR—COOH$	R—	Amount of Amino Acid per 100 g Protein	
		Collagen	Gelatin
Nonpolar			
Glycine	—H	27.2	26.9
Alanine	$—CH_3$	9.5	9.3
Valine	$—CH(CH_3)_2$	3.4	3.3
Leucine	$—CH_2—CH(CH_3)_2$	5.6	3.4
Isoleucine	$—CH(C_2H_5)CH_3$		1.8
Proline (amino acid)	$—CH_2—CH_2—CH_2—$	15.1	14.8
Methionine	$—CH_2—CH_2S—CH_3$	0.8	0.9
Phenylalanine	$—CH_2—C_6H_5$	2.5	2.55
Polar			
Tyrosine	$—CH_2—C_6H_4—OH$	1.0	1.0
Serine	$—CH_2OH$	3.37	3.18
Hydroyproline (amino acid)	$—CH_2—CHOH—CH_2—$	14.0	14.5
Treonine	$—CHOH—CH_3$	2.28	2.2
Basic			
Arginine	$—(CH_2)_3—NH—C(NH_2)=NH$	8.59	8.55
Histidine		0.74	0.73
Lysine	$—(CH_2)_4—NH_2$	4.47	4.6
Hydroxylysine	$—(CH_2)_3—CHOH—CH_2—NH_2$	1.1	1.3
Acid			
Aspartic acid	$—CH_2COOH$	6.3	6.7
Glutamic acid	$—(CH_2)_2COOH$	11.3	11.2

Source: B. V. Deryagin and S. M. Levy, *Film Coating Theory*, Focal Press, London, 1964, p. 90. (By permission of Focal Press, London.)

gelatin molecule. At a certain solution condition, at the isoelectric point of the gelatin, the number of $-\overset{+}{N}H_3$ and the number of $-COO^-$ are equal, and the molecule has a net charge of zero. The isoelectric point, which is characteristic of the kind of gelatin, its method of preparation, and the impurities present, is the point at which the gelatin molecule is most tightly coiled because of the equal number of charge attractions. It is the condition of acidity or alkalinity at which the gelatin molecule is least soluble in water. The molecule length is a minimum because of the attraction of the neighboring opposite charges. For lime-processed gelatins, the isoelectric point lies on the acid side; for acid-processed gelatins, the isoelectric point occurs in slightly alkaline solution.

Under conditions more acid than the isoelectric point, the gelatin molecule becomes positively charged, because the amino groups exist as $-\overset{+}{N}H_3$ and the carboxylic acid groups as $-COOH$. Because of the repulsion of the like positive charges, the gelatin molecule uncoils slightly and becomes more soluble. In solutions more alkaline than the isoelectric point, the gelatin molecule becomes negatively charged. The amino groups exist as $-NH_2$ and the carboxylic acid groups as $-COO^-$. Again, because of the like negative charges, the gelatin molecule expands from its state at the isoelectric point. Thus, the exact conditions of the solution of the gelatin molecule influence its properties as a medium to suspend silver halide microcrystals, which may be negatively or positively charged depending upon the pH. (See Figure 4.)

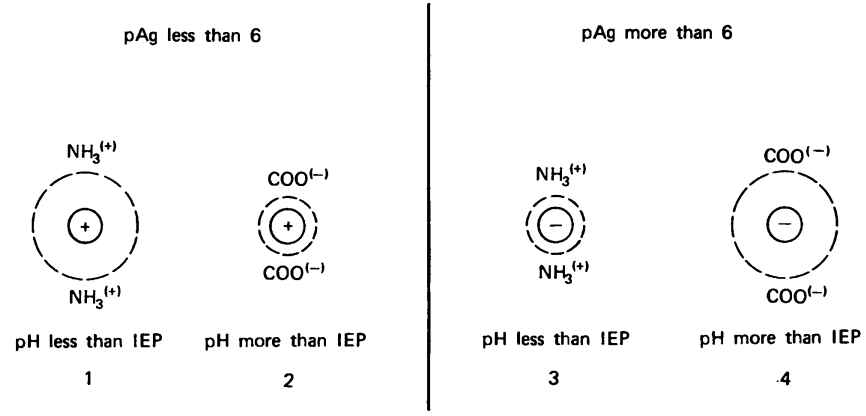
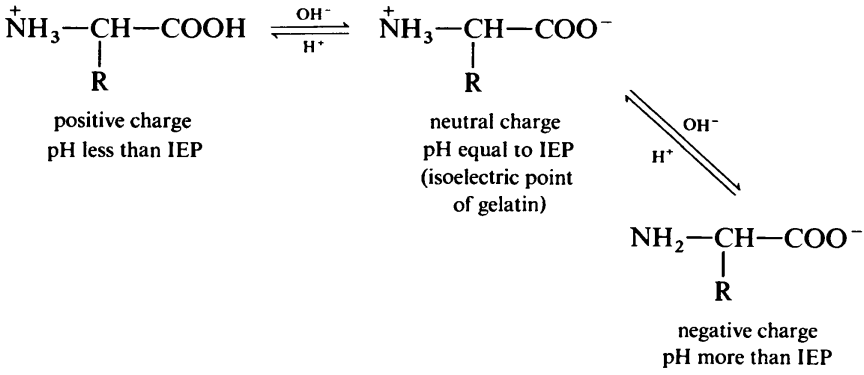


Figure 4. Scheme of repulsion or attraction of gelatin molecules on silver halide molecules. Adapted from E. Klein, E. Moisar, and E. Roche, in *Photographic Gelatin*, edited by R. J. Cox, Academic Press, New York, 1972, p. 225.

The effect of pH on the charge of a gelatin molecule may be shown as follows:[108]



The repulsion or attraction between molecules of gelatin and silver halide is shown in Figure 4.

1. At low pAg the silver halide crystal is charged positively, and positively charged gelatin (at low pH) is repulsed, allowing an increase in the growth rate of the crystal.
2. At low pAg and high pH values, the negatively charged gelatin is attracted by the positively charged crystal, blocking the surface and decreasing the crystal growth rate.
3. At high pAg, the crystal is negatively charged by adsorbed halide ions, attracting the positively charged gelatin at low pH and inhibiting crystal growth rate.
4. At high pAg and pH, crystal growth rate increases, because the negatively charged crystal repels the negatively charged gelatin.

Other Constituents of Gelatin

The exact composition of gelatin is determined by the protein from the animal source and the treatment of the collagen to secure the gelatin. Because it is almost impossible to control precisely every variable in the composition of the protein and its treatment, gelatin remains a somewhat variable product, not a consistently pure chemical. Minute impurities are present. The effective impurities are essentially of two types: those that enhance the light sensitivity of the silver halide suspended in the gelatin and those that act as restrainers.

Sensitizers in Gelatin

The sensitivity of early gelatino-silver halide emulsions was due in large measure to the presence on the silver halide microcrystals of impurities

derived from the gelatin. The impurities were present in such small quantities that their presence was long undetected. But in 1925 S. E. Sheppard[32–34] reported that a gelatin impurity, which he called Gelatin-X, was similar in effect to allyl mustard oil (allyl isothiocyanate). Quantities of from one part in 300,000 to one part in 1,000,000 parts of the gelatin were sufficient to increase enormously the light sensitivity of the silver halide. Sheppard concluded that allyl isothiocyanate was the impurity in gelatin that produced the increase in light sensitivity, and he went on to show that other sulfur compounds containing the group also produced this effect. This discovery of the chemical sensitization of silver halide emulsions was an important milestone that has led to today's high-speed photographic materials.

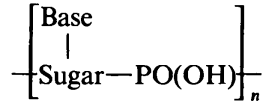
Other investigators have felt that allyl isothiocyanate was not the sulfur-containing sensitizer present in gelatin. A. Steigmann[35,36] suggested that the sulfur sensitizers of gelatin were thiosulfates derived from the amino acid cystine, a trace amount of which is present in gelatin. In 1952 Henry W. Wood[37] found "that the natural sensitizer is a thiosulfate or a compound with very nearly the same properties," thus confirming the earlier supposition of Steigmann. Radioactive thiosulfate was used by D. M. Spracklen[38] to show that the thiosulfate first is adsorbed to the grains of a silver halide emulsion, then breaks down to form silver sulfide during the finishing treatment. Tetrathionate does not exist in commercial gelatin.[39] Because of the importance of the sensitizing action of thiosulfate, its levels must be controlled in gelatins. Considerable effort is being devoted to devising analytical methods for the detection of the trace quantities of thiosulfate in various samples of gelatin.[40–48] Carbohydrates are known to be present in gelatin extracts from proteins, and such compounds may form bisulfite compounds that could liberate sulfur dioxide. The sulfur dioxide might give rise to thiosulfate or other sulfur sensitizers.[49]

H. W. Wood[50] has observed: "It seems likely that, owing to the complexity of living organisms, the discovery in them of new classes of chemical compounds will be never ending. Traces of these compounds are then also to be expected in derived materials such as gelatin." Wood studied the sialic acid (probably *N*-acetyl neuraminic acid) content of gelatin. Albert Steigmann[51] was one of the first to study the presence of aldehydes in gelatin. Aldehydes are reducing agents, so their reactivity may account for some of the sensitizing or fogging properties of gelatin.[52,53] J. N. Armes[54] found that the amount of aldehyde, depending upon the gelatin, varied from 17 to 600 parts per million of gelatin (expressed as glyceraldehyde). All the aliphatic aldehydes in gelatin were found to be present in a reactive form and partly as *N*-terminal groups.

Nitrite is also a contaminant in some gelatin, although its presence may not have any photographic effect.[55] The compound may be involved with the formation of a fogging agent.

Restrainers in Gelatin

There are, however, substances in gelatin that have a restraining action upon the sensitivity of a photographic emulsion, decreasing fog and increasing image contrast. Their presence was first pointed out by Albert Steigmann[56] in 1927, and he sought to identify their nature.[57–66] Steigmann later suggested that the restraining compound was nucleic acid.[67] The presence of nucleic acid in photographic gelatin has been claimed,[68,69] but most of the identification tests have been for the components of nucleic acid, not for the acid, or a nucleoside or a nucleotide, of which the components might be a part. Nucleic acid is a general term, covering many acids of varying composition, but all contain a purine or pyrimidine base united to a sugar (ribose or deoxyribose), which is joined to a phosphate group.[70] The base and sugar form a nucleoside, and this combined with the phosphate forms a nucleotide:



P. S. Gordon and E. D. Swann[71,72] found that "the restraining substances contain purine groups and are nucleic acid fragments, not the nucleotides." Hide gelatins were shown to have a higher content of adenine, a nucleic acid component, than bone gelatins.[73–76] Adenine, guanine, hypoxanthine, xanthine, and deoxyribose nucleic acid have been found to affect the photographic behavior of gelatin.[77] Gelatin containing only negligible amounts of nucleic acid still may exhibit restraining action.[78] The activity of most restrainers increases with increasing alkalinity.[79–80]

Purification of Photographic Gelatin

Gelatin is not a pure chemical but the general name given to a variable raw material. For photographic purposes it would be desirable for gelatin to possess neither sensitizing nor restraining actions—that is, to be inert. The precise modification of the gelatin could then be accomplished by the emulsion maker. Hydrogen peroxide treatment of gelatin as a bleach was suggested by S. E. Sheppard,[81] but decomposition of the gelatin must be avoided and all of the peroxide must be removed. The amino acid methionine has been reported to be converted to methionine sulphoxide by peroxides or

oxidizing agents.[82] The removal of both speed-increasing and speed-decreasing microconstituents from gelatin must be done carefully if undesired degradation and impurities are to be avoided. Calcium hypochlorite or sodium peroxide have been said to be suitable for preparing inert gelatin.[83]

The removal of impurities from commercial photographic gelatins may be accomplished by a number of treatments, and these have been reviewed by Walter D. Kelly, Jr.[84] Soluble organic and inorganic impurities may be removed by water washing. Treatment with ion-exchange resins would remove ionic impurities.[85–87] Activated carbon has been used to remove impurities by adsorption to the surfaces of the carbon.[88] Oxidizing agents, such as hydrogen peroxide or peroxyacetic acid, can destroy impurities more easily oxidized than the gelatin itself. According to Kelly, washing and de-ionizing did reduce the sensitizer level of gelatin, but oxidation with peroxides produced the most inert gelatin. Treatment with peroxyacetic acid was found to be the most effective. Alkaline hydrogen perioxide was next in effectiveness, but the gelatin was badly degraded.

A. G. Ward[89] has noted: "The preparation of sufficiently pure collagen for the amino acid composition to be regarded as representative has presented an almost impossible task." Yet, gelatin has a number of desirable functions, some not yet completely understood, that have made the task of purification necessary.[90–92]

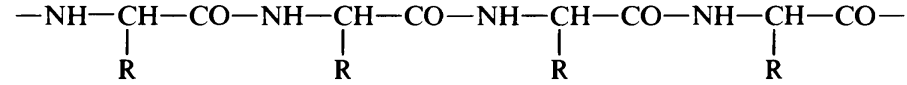
Properties of Photographic Gelatin

1. A transparent vehicle to adhere the silver halide microcrystals (and the silver of the final image) as a protective layer on a support, such as glass, paper base, or plastic films.
2. A protective medium (a colloid, from the Greek work for glue[93]) to keep the silver halide microcrystals in colloidal suspension and prevent coagulation. Gelatin adsorbs strongly to silver crystal surfaces, although there is question whether the adsorbed layer is one molecule in depth or a double layer.[94–98] Research by H. G. Curme and C. C. Natale[99] and others[100] suggests that the random coils of gelatin are more compact when adsorbed onto crystals and extend perpendicular to the crystal surface.
3. A factor in determining the size and shape of silver halide crystals during their precipitation and maturation.[101–109] Without gelatin, crystal growth is fast, producing globular crystals; with gelatin, crystal growth is slower, yielding flat platelets.
4. A chemical sensitizer of the silver halide crystals. Microimpurities, some known and others not yet recognized, or the presence of groups in the gelatin molecule, can increase or decrease the light sensitivity and gradation of the photographic emulsion.[110–112]

5. A reactive chemical, being both an acid and a base at the same time. The gelatin molecule binds gold, silver, and other metal ions.[113–115] The interaction of the carboxyl groups of the gelatin molecule with trivalent ions, such as chromium or aluminum, decreases the water solubility of the gelatin layer.[116] Aldehydes react with the amino groups of gelatin,[117] causing a hardening of the emulsion layer through crosslinking of the amino groups of gelatin molecules.
6. An easily coatable substance, changed from a solid to liquid to solid by a moderate change in temperature.[118–123] Gelatin can be dissolved in hot water or rapidly chill-set before drying. Removing most of the water from the emulsion produces a flexible, nontacky layer that is stable during storage.
7. A remarkably pure substance, better than 99.95% pure. Photographic gelatin is much purer than most photographic chemicals and is far purer than food-grade gelatin.
8. An acceptor of bromine or chlorine formed during light exposure, thus preventing a fading of the latent image[124–128]; the gelatin layer is also a good oxygen barrier.
9. An influence on the development process.[129–130] Gelatin slows the rate of development, possibly through its adsorption on the surface of silver halide crystals or by reaction with silver ions of the crystal. In the presence of gelatin, developed silver is more filamentary, having superior light-stopping power, and the silver image is of a neutral tone.

Gelatin Substitutes

The lengthy procedure of preparing, purifying, and blending batches of gelatin obtained from the bones of cattle from India, or the hides of cattle from Argentina, or the skins of pigs from the United States, has made desirable a synthetic substitute for gelatin in photographic materials. Gelatin may be pictured as having a general structure of the following form:



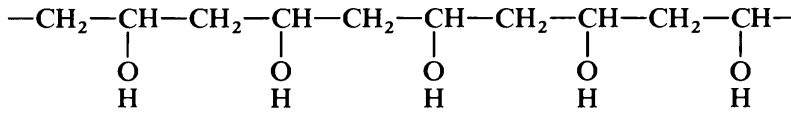
where the R represents side chains formed from one of the 18 amino or imino acids present in gelatin. Some of the R groups are derived from lysine, where R is

$$-CH_2CH_2CH_2CH_2NH_2,$$

or glutamic acid, where R is $-CH_2CH_2COOH$.

Gelatin is a natural polymer, but synthetic polymeric molecules are now routinely prepared for many uses. It would seem advantageous to prepare synthetically a polymer related to gelatin, having gelatin's desirable features, but free of batch-to-batch variations. Such a water-soluble synthetic polypeptide has been prepared primarily from glutamic acid and lysine with the presence of glycine, proline, cystine, phenylalanine, or sarcosine. In patents by Henry Walter Wood,[131–133] synthetic polypeptides were claimed to permit growth of silver halide crystals after precipitation in the polymer. Other synthetic polymers having both free amino groups and free acid groups have been described.[134–135]

Numerous polymers have been investigated as replacements for gelatin.[136] Polyvinyl alcohol has been used more extensively than any other in the past. This polymer can be represented simply by the structure



Polyvinyl alcohol (PVA) has been used commercially in slow-speed black-and-white photographic paper[137] and in color release film for motion pictures,[138–140] but these uses have not continued because of deficiencies.[141] Because of its potential use, PVA or modifications of it have been extensively investigated.[142–147] Hardening PVA layers is difficult, although boric acid is known to react with compounds containing hydroxy groups.[148] Hardeners, however, must be chosen carefully to avoid a detrimental action. The combination of melamine and formaldehyde has been said to be suitable.[149] Polyvinyl alcohol is known to interfere with the growth of silver halide crystals, thus limiting the photographic speed of the photographic emulsion.[150] One method[151] proposed has involved the precipitation of the silver halide in gelatin so modified as to be compatible with PVA; another[152] has involved the treatment of the emulsion at high temperatures in the presence of a nitrogen base. Modification of PVA has been proposed to permit improved hardening of coated emulsions.[153]

Replacement of all of the gelatin in photographic layers by cellulose derivatives, polyvinyl pyrrolidone, polyvinyl acetate, polymethylacrylamide, and a variety of other polymers has been the subject of a large number of studies and patents.[154–176] Polymers have found extensive use also for replacing part of gelatin.[177–181] Such a replacement often allows less silver to be present for obtaining an image of normal characteristics and often decreases the differences between wet- and dry-developed silver images.[182–190] A review of the considerable work on these polymers is given by Kiyoshi Murofushi.[191]

Binderless Silver Halide Materials

The physical and purity limitations of gelatin, gelatin substitutes, and replacements has lead to efforts to use evaporated silver halide without a colloid binder as the recording photographic medium.[192,193] Daguerre used a silver iodide plate without gelatin at the beginning of photography. The concept of applying heat to evaporate silver halide upon a moving film base under vacuum conditions is not new, having been studied in the 1930s.[194,195] Securing uniform coatings of high purity has been a technological challenge.[196] Modern research, however has provided much information concerning the very pure, thin-layer (optimum: 0.3 μ thickness)[197] silver bromide evaporated films. The sensitivity is very low, a characteristic of the Daguerreotype plate as well. Vacuum-depositing a metal, such as zinc or copper, increased the sensitivity 10 times, up to 0.1 ASA Index unit.[198] Development times are rapid, from 10 to 30 sec, in conventional developing compositions that contain inert gelatin or hydroxyethylcellulose. High-solvent developing solutions cannot be used. Image resolution for electron-beam recording has been said to be roughly 200 lines per millimeter.[199] Evaporated silver bromide films have been reported to be variable in speed upon storage, subject to fog growth, and grainy when the image is developed. Improvement in characteristics has been claimed by using a gelatin overcoat on the evaporated film, the gelatin or other vehicle containing speed-increasing and fog-decreasing chemicals of the types found beneficial in conventional silver halide materials.[200] Extensive research on binderfree films has been carried out by James E. Lu Valle et al.[201] as well as by others.[202]

Binderless silver halide systems have also included treating silver foils to convert some of the metallic silver to silver halide.[203]

MAKING A PHOTOGRAPHIC EMULSION

The preparation of a photographic emulsion is now almost an applied science. In the early, empirical days it was an art practiced only by the experienced. In his book, *Photographic Emulsion Technique*, T. Thorne Baker[204] tells how the trained eye of the old-time master emulsion chemist could detect the correct time to stop "cooking" an emulsion in the kettle. As the heating continued, the emulsion color turned from yellow to greenish-blue, as viewed by transmitted tungsten light. At the blue stage the grain size of the emulsion had reached the maximum sensitivity. Allowing the grains to grow to produce colors of bluish-violet or gray would not increase sensitivity but would produce detrimental emulsion characteristics. In contending with chemical uncertainties, such as the variability of the gelatin, visual

observation proved valuable. But modern emulsion-making practices use every available technological aid in attempting to reduce the art to a reproducible science.

The full science of making and coating photographic emulsions is one of the most closely held of industrial secrets. The preparation of photographic emulsions, especially those used in color photography, is a small miracle of photographic chemistry, and very few details have been revealed. This practice of secrecy was said to have started as early as 1882.[205] The standard reference book is still E. J. Wall's *Photographic Emulsions*—and this book was published in 1929.[206] More recent are *Photographic Emulsion Technique* by T. Thorne Baker,[207] *Making and Coating Photographic Emulsions* by V. L. Zelikman and S. M. Levi,[208] and a book reprinting a series of publications during the years 1927 to 1934 under the guidance of B. H. Carroll.[209] Part Two, Volume 1, of *Photographic Chemistry* by Pierre Glafkides[210] contains formulas and methods of preparation of various types of photographic emulsions. Publications by A. Steigmann,[211–212] T. Thorne Baker,[213–215] and H. W. Greenwood[216] contain specific formulations, whereas articles by F. Dersch[217] and F. W. Mueller[218] are more general. An article by Thomas T. Hill[219] has typical formulas with mixing instructions for simple emulsions. But the published literature on the subject of making photographic emulsions is either old or limited or both, and sometimes misleading, although some modern techniques described in patents are tantalizing.

Modern industrial practices have made emulsion preparation into a rapid and continuous procedure. It may, however, be considered to have five distinct stages:

1. Formation of the silver halide crystals.
2. Growth of the crystals to an optimum size.
3. Removal of undesirable chemical by-products.
4. Increasing the sensitivity of the crystals by chemical additions.
5. Preparation of the finished emulsion for coating.

Formation of the Silver Halide Crystals (Nucleation and Initial Growth)

The silver halide crystals are formed by mixing a soluble silver salt, usually silver nitrate, with a soluble halide salt or salts in a water solution containing gelatin. In this step, called emulsification, the sodium, potassium, or ammonium salts of any of the three halogens may be used as the halide salt. In the single-jet method of preparation, a silver nitrate solution is run, at a carefully-controlled rate, from a jet into an agitated solution containing the halide salt and the gelatin. The double-jet method adds the solution of silver nitrate

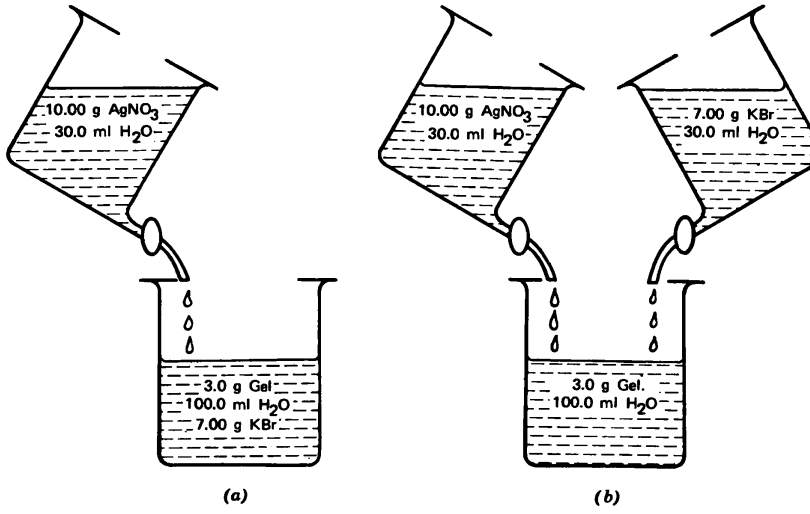


Figure 5. Precipitation of silver bromide by (*a*) the single-jet method and (*b*) the balanced double-jet method. [C. R. Berry, S. J. Marino, and C. F. Oster, Jr., *Phot. Sci. and Eng.*, 5: 332 (1961)]

from one jet and the equivalent solution of the halide salt from another jet into a stirred gelatin solution. (See Figure 5.) However, many, many procedural variations exist in this first step of emulsion making. One method of importance involves adding the entire halide solution quickly to the silver nitrate.

The solubility of silver ions and halide ions in the same aqueous gelatin solution is extremely low. The solubility of silver chloride is so low that chloride ions are often used in chemistry to precipitate silver ions quantitatively from water solutions. Silver chloride is soluble, however, to the extent of 0.0018 g in a liter of water at 25°C.[220] Silver bromide is less soluble than silver chloride, and silver iodide still less soluble. (See Table 2.)

Table 2. Solubility of Silver Halides in Water

Halide	Solubility (g/liter, 25°C)
Silver chloride	0.00181
Silver bromide	0.000134
Silver iodide	0.00000470

In the making of the emulsion the solubility of the silver halide in the gelatin solution is instantaneously exceeded. The solution first becomes cloudy from the precipitation of the microcrystals of the silver halide, then turns milky and opaque as the crystal growth proceeds. Under these conditions of forced crystal growth, the rapid formation of the ordered crystal lattice may be less than perfect. Coalescence of nearby crystal particles, producing a grain with built-in boundaries and other defects, is not a major factor in the presence of gelatin but may occur with other emulsion vehicles. If present, ions (other than silver) that form halide salts of low solubility will be built into the crystal lattice.

At the very start of the mixing of the solutions of silver nitrate and potassium bromide there is an instant, said to be within a hundredth to a thousandth of a second, before the solution reaches a critical supersaturation.[221–222] Nucleation of the crystals is over within 60 sec, according to R. W. Berriman[223] or C. R. Berry and D. C. Skillman.[224] Others[225] have concluded that after 60 sec "it is likely that nucleation continues in the region of the silver nitrate jet and the nuclei formed there grow by coalescence to perhaps 0.1 μm before being swept into the bulk of the vessel." As long as the silver nitrate is being added, there is a level of supersaturation of the insoluble silver halide. After the silver nitrate has all been added, the supersaturation is no longer present.

Crystal growth takes place on the nuclei and small crystals. A range of crystal sizes is present, and the fine crystals are more soluble than the large ones. Under the conditions of the emulsion precipitation, the fine crystals dissolve and reprecipitate upon the coarser crystals. This is the process of physical or Ostwald ripening. During Ostwald ripening a competitive growth process has been observed among crystals of different structure.[226] The presence of silver halide solvents affects the growth rate significantly. Reducing the iodide level or increasing the concentration of ammonia increases growth rates.[227,228] Mild Ostwald ripening tends to convert cubic crystals to spheres. Different environments produce different shapes of silver bromide microcrystals during rapid Ostwald ripening.[229] (See Figures 6 and 7.)

Many silver bromide grains consist of large parallel triangular or hexagonal faces and narrow lateral faces. These lateral faces exhibit the greatest rate of growth and also the fastest degradation rate. In a supersaturated solution silver bromide is deposited preferentially on the narrow lateral faces, producing crystals that are flat. The silver bromide is deposited only very slowly on the large flat surfaces. The solubility of silver bromide is higher from the narrow lateral faces than from the large, flat top or bottom surfaces. According to R. Matejec,[230] "When AgBr grains are brought into contact with saturated AgBr complex solutions, the result is an AgBr concentration

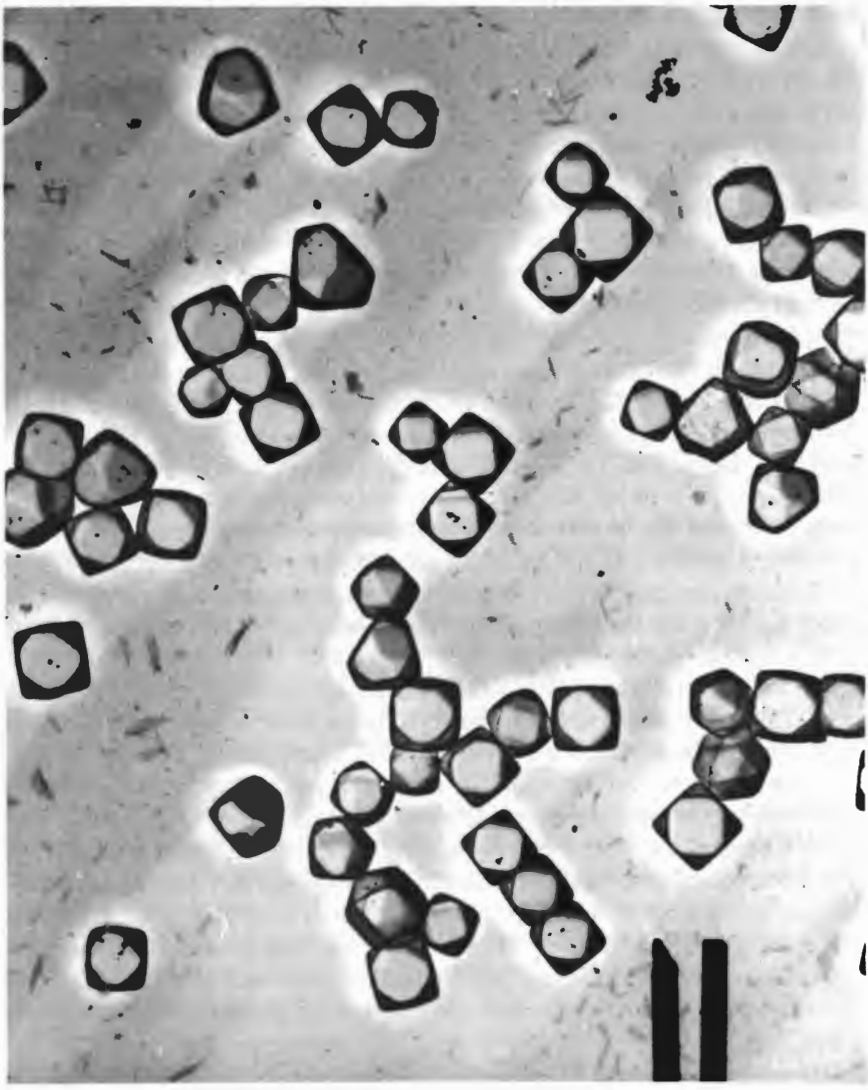


Figure 6. Cubo-octahedral crystals of silver bromide before Ostwald ripening. (6000 x)

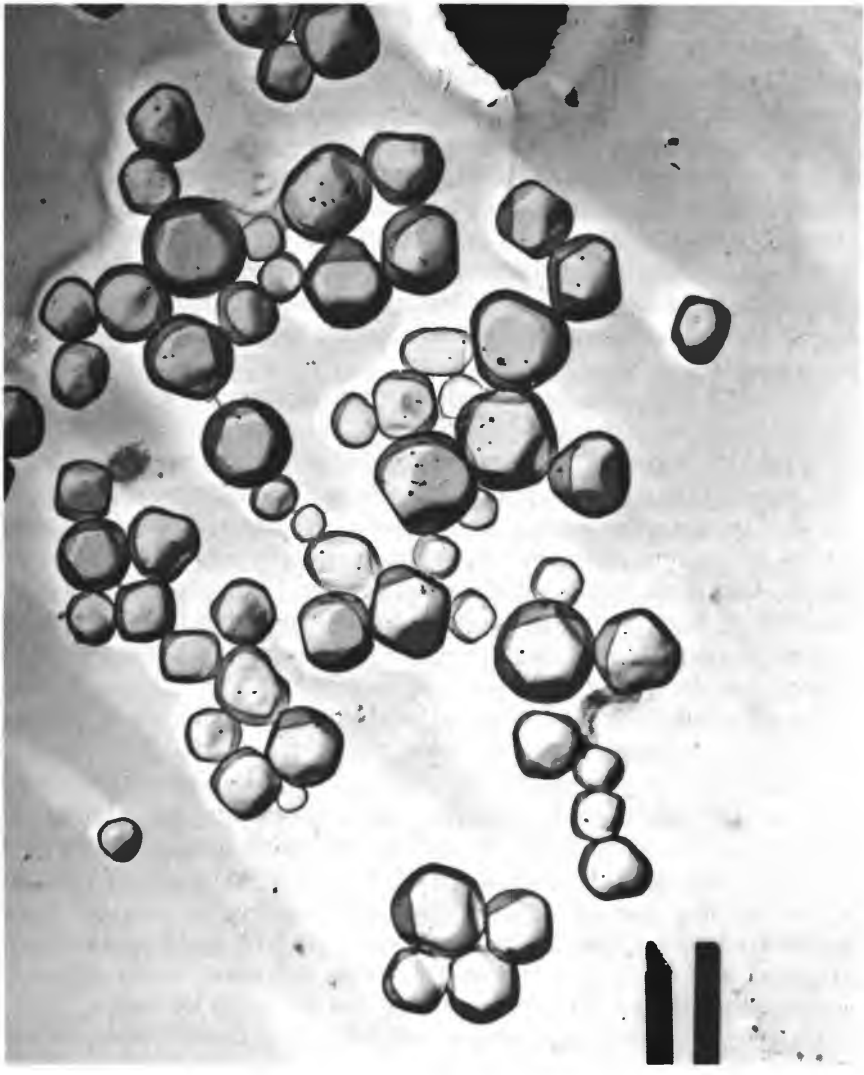


Figure 7. Same silver bromide crystals as in Figure 6 after Ostwald ripening for 200 min at 50°C (pAg 9.9). (6000 ×) [C. R. Berry and D. C. Skillman, *J. Phot. Sci.*, 16: 137 (1968)]

in the solution, which ranges between the saturation concentrations of the two types of faces: A physical ripening of the faces occurs which conveys AgBr from the crystal faces of higher solubility (narrow lateral faces) to faces of lower solubility (large top and bottom faces). Thus the flat-shaped AgBr grains are converted to compact grains."

Most emulsion precipitates contain a mixture of halides. In this case a complex recrystallization can occur.[231] Recrystallization occurs during Ostwald ripening and can reduce the size of large crystals. Recrystallization is believed responsible for the irregular crystal shapes seen in silver halide precipitates.[226] Recrystallization phenomena can build foreign ions into the crystal and thus produce sensitivity centers for the increased sensitivity of the crystal.

The single- or double-jet method of emulsion preparation offers almost infinite variability of the characteristics of the emulsion. Slow addition of the silver nitrate solution allows a smaller number of crystals to grow to a larger size; rapid addition produces a greater number of small crystals of similar size that do not grow rapidly. Higher solution temperatures of the silver nitrate, halide, and gelatin accelerate the increase in grain size. But a high degree of agitation during crystal formation favors the production of smaller grains. C. R. Berry and S. J. Marino[232] found that "an increase in the time of precipitation increased the homogeneity of the crystals in the double-jet method, just the reverse of the single-jet method."

The extent and type of the excess of halide ions present during the precipitation has a profound effect on emulsion characteristics. In single-jet preparation the silver ions are added slowly to all of the halide ions in the gelatin solution. The quantity of halide ions decreases continuously during the grain formation. In the double-jet method essentially equal concentrations of the silver and halide ions are added simultaneously to the gelatin solution, which also may contain some halide ions. Excess halide ions act as an accelerator to grain growth. Thus, the initial crystals formed by the single-jet preparation in the large excess of halide ions will grow rapidly, acting as crystallization centers for the silver halide that will be added later.

The type of halide ions present at any stage of the crystal formation also influences grain growth and sensitivity. The addition of silver nitrate to a gelatin solution containing bromide and iodide ions precipitates silver iodide first, according to C. R. Berry and S. J. Marino.[3] Haruhiko Iwano[233] found that "When silver halide mixed crystal grains are produced by running silver ions into a solution of a mixture of halide ions, the first additions of silver ions cause the least soluble component of the mixture to precipitate first; that is, pure silver iodide in silver bromo-iodide system."

Crystals are formed containing ions of the various silver halides distributed according to the laws of chance. In the single-jet method more iodide

ions may be present near the core of the crystal because of their limited quantity. Silver iodide may also be introduced in such a manner as to be incorporated into the lattice throughout the crystal. Because the iodide ion is larger than the bromide or chloride ions, the presence of the iodide puts a strain on the lattice structure, producing defects that result in higher photographic sensitivity to light.

The excess of halide ions during crystal formation acts as a solvent to dissolve small grains and promote the growth of the larger crystals. The presence of other silver solvents during the emulsion preparation also will influence grain growth and sensitivity. Ammonia is an excellent solvent for silver ions. The ammonia may be added to the silver nitrate solution, the halide solution, or the solution that contains the gelatin. When ammonia is first added to the silver nitrate, silver oxide precipitates. But the continued addition of ammonia dissolves the silver oxide to produce a soluble silver-ammonia ion. Grain growth is rapid when the silver halide is formed in the presence of ammonia, permitting the use of lower temperatures in the preparation of ammoniacal emulsions. In the neutral emulsions containing only the halide ions as the silver solvent much higher temperatures must be used to insure suitable grain growth. This type of emulsion is sometimes referred to as "boiled" because of the need for higher-temperature treatment.

The kind and the purity of the gelatin control grain growth and influence grain sensitivity. Gelatin is only weakly attached to the surface of the silver halide crystals as they are formed. This weak attraction, called adsorption, is sufficient to coat the grains to keep them separated and in suspension. But this weak adhesion of gelatin, unlike the adhesion of many synthetic gelatin substitutes, allows the crystal growth so necessary for higher photographic sensitivity. Impurities in the gelatin also may influence grain growth as well as supplying sensitizing substances for increased grain sensitivity. Impurities are deliberately added to gelatin solutions to affect grain growth and sensitivity or to influence the rate of development or fixation.

Growth of Crystals to Optimum Size

The single or mixed-halide silver grains grow considerably during the initial precipitation of the crystals of the emulsion. The second stage of the emulsion preparation, called physical ripening or ripening, involves grain growth by maintaining the emulsion preparation at an elevated temperature. Silver halide solvents must be present for the ripening to proceed. Some of these ripening agents were produced during the formation of the silver halide grains. Excess halide ions, either those already present or those added additionally at this stage, or ammonia or ammonia derivatives, or other silver halide

solubilizing compounds, are often used for promoting the growth of the silver halide grains during the continued heat treatment.

Because of the variable nature of the composition of the grains, some crystal lattices will be dissolved more easily than others. The ripening agents solubilize the surface silver ions of these more readily attacked grains, reprecipitating the silver on the less soluble grains. Generally, the smaller crystals are less stable than the larger ones; thus the small crystals tend to be redistributed onto the larger grains, producing the grain growth needed for maximum sensitivity.

This cannibalism of the small grains by the larger, more stable grains is sometimes used to produce practical emulsions of desirable properties. After the normal grain growth during ripening has been completed, a further precipitation of silver halide is made. These new grains are small in comparison to the fully ripened grains. The small grains dissolve and deposit on the larger grains after another period of heating. The final silver halide grains may have jackets of silver halide that are considerably different than the interior cores.

Removal of Undesirable Chemical By-Products

The addition of silver nitrate to potassium bromide to produce silver bromide also yields potassium nitrate as a by-product. After the grains have been grown to the desired size, excesses of other compounds may be present. These compounds may not interfere when the emulsion is coated on paper base; in the past, indeed, many "unwashed" emulsions were so used. But the coating on film base of an emulsion with its by-product salts may result in the salts' crystallizing when the coated emulsion layer is dried. Some salts tend to cling to water, making drying difficult. And high-speed negative film emulsions will require additional treatment to secure the desired sensitivity. This further treatment is inhibited by the presence of excess halide ions, ammonia, or other compounds still retained in the ripened emulsion preparation.

The classical method of removing the undesired compounds was to wash the emulsion preparation with water. The emulsion was set to a stiff jelly, often after additional gelatin had been added. The jelly was then forced through a grid to give shreds called noodles, which were washed in cool running water. The water often contained calcium or magnesium salts, compounds that minimized the swelling of the gelatin, because any uptake of water produces an undesirable dilution of the emulsion. The by-product salts in the noodles diffused very slowly, especially into water containing the nonswelling compounds. A long period of washing requiring a large volume of water was necessary to reduce the emulsion salts to a sufficiently low concentration for the further treatment of the emulsion.

This slow diffusion of the undesired soluble salts from the noodles was

much too time consuming to be adaptable to industrial methods. Sometime before 1940 emulsion makers secretly began to use a much more rapid method. As early as 1934 in Germany sodium sulfate was reported to have been added to emulsion preparations. This salt caused the gelatin to coagulate and separate from the warm aqueous phase. The silver halide grains were carried down in the curds of gelatin. This separation of the gelatin–silver halide from the water solution must be very carefully controlled to prevent the clumping of the silver halide grains, but the separation is rapid, almost complete, and far more useful for industrial emulsion preparation. The aqueous phase can be removed by decanting or other methods. The coagulated emulsion may be soaked in a number of changes of cold water, if necessary. The emulsion curds are then dispersed in water by adding sufficient alkaline compound to raise the solution above the isoelectric point of the gelatin. After redispersion the emulsion may again be precipitated and the liquid separated to further reduce the undesirable soluble salts. Each washing, settling, and decantation step does require time, however. As a means to speed the removal of the undesirable salts the use of centrifugal force has been proposed[234,235] to separate the flocculated emulsion from the liquid phase.

The salt precipitation of a protein, such as gelatin, can be carried out with a number of compounds that contain double- or triple-charged ions. A 1929 patent of Raymond H. Lambert[236] proposed the use of the nitrates of tin, lead, titanium, cerium, thorium, zirconium, germanium, and others. Ammonium sulfate was patented in 1939.[237] Tri- and tetravalent metal ions harden gelatin and make the resuspension of the silver halide difficult. It was proposed[238] to add an acid (acetic, citric, sulfuric, phosphoric, and others) and a variety of salts (calcium nitrate, magnesium sulfate, sodium sulfate, zinc nitrate, and many others) to coagulate the silver halide. If the process is carried out near the isoelectric point of the gelatin, some of the gelatin is coagulated as well, but the gelatin is not hardened. Considerable amounts of the salts must be used, and they must be removed from the precipitate by washing.

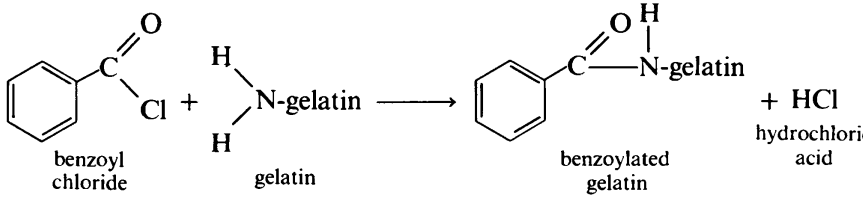
There are other methods to separate the silver halide-gelatin from the water phase of the emulsion preparation. On the acid side of the isoelectric point the gelatin will lose its water solubility if its free amino groups are no longer available to produce that solubility. Acids will react with gelatin amino groups to form a salt. Trichloroacetic acid[239] or partial esters of a phosphoric acid[240] have been patented as flocculants for gelatin–silver halide emulsions. Long-chained alcohol and acids, such as lauryl hydrogen sulfate or the sodium salt of alkyl naphthalene sulfonic acid, called anion soaps, also precipitate gelatin–silver bromide emulsions.[241–242] Once the acidic part of the anion soap has reacted with the amino group of the gelatin, the long water-insoluble chain of the anion soap adds to the insolubility of the complex with the gelatin. The last residues of the soaps are difficult to remove by washing.

Organic solvents have been suggested for dispersing the coagulated silver halide–gelatin sediment.[243] Organic solvents themselves will coagulate silver halide emulsions, but they are costly and may not remove all the water from the flocculated emulsion.

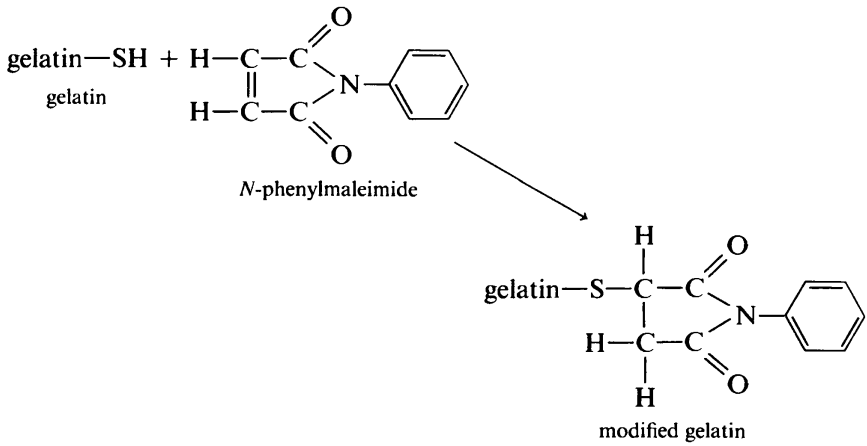
Many types of acidic compounds have been used to flocculate silver halide emulsions. The curds are then dispersed in water by adding a sufficient amount of an alkaline compound to raise the solution above the isoelectric point of the gelatin. The acidic flocculants are often polymeric acids. In 1951 Edward C. Yackel[244–245] patented high-polymer compounds containing carboxyl groups. Other compounds have been patented: gelatin–acrylic acid graft polymers,[246] sulfonated copolymers of styrene with vinyl compounds,[247] or linear copolymers of *N*-vinyl compounds with acrylic or methacrylic acids.[248] Flocculating agents have been prepared from copolymers of 4-vinylpyridine sulfonic acid or 4-vinylpyridine disulfonic acid with acrylic acid or styrene sulfonic acid.[249] Other polymers have also been patented.[250,251] Silver halide may be dispersed in gelatin, centrifuged, and then dispersed in a water-soluble cellulose ester.[252]

The desire of emulsion makers to facilitate the coagulation of the gelatin–silver halide into curds has led to the direct modification of the gelatin itself. As already described, an acid can be added to form a salt with the amino groups of the gelatin, and the amino group then is not available to make the gelatin soluble in acidic solution. Instead of this salt formation, the amino groups may be reacted with suitable acids to make permanent modifications; this type of treated gelatin is not able to be soluble under acidic conditions. Addition of enough acid to lower the gelatin just below the isoelectric point causes the modified gelatin–silver halide to coagulate to an easily separable curd. Care must be taken to insure that grain clumping does not occur when the curd is again dispersed in water. The modified gelatin may have been present from the first precipitation of the silver halide grains or may have been added after the treatment to promote grain growth. The adsorption of the gelatin to the surface of the silver halide grains does not appear to have been affected by the modification of the gelatin.

Derivatives of gelatin can be prepared by reacting photographic gelatin with a number of compounds, such as sulfonyl chlorides, benzene sulfonyl chloride, carboxylic acid chlorides such as phthalyl chloride, acid anhydrides such as phthalic anhydride, isocyanates such as phenyl isocyanate or 1,4-diketones such as acetonyl acetone.[253–269]



Improved gelatin derivatives have been claimed[270] when a compound containing one or more sulfonylfluoride groups is reacted with the gelatin rather than using a compound with sulfonylchloride groups. Halogeno-1,3,5-triazines are also said to react with gelatin to provide suitable derivatives for coagulation of a photographic emulsion at or below the isoelectric point of the gelatin.[271] Pigskin gelatin has been chemically modified by attachment of sulfoalkyl or carboxymethyl groups to the gelatin molecule.[272,273] Instead of forming gelatin derivatives by reacting with the amino groups of the gelatin molecule, suitable derivatives may be made by reacting with the —SH groups of the gelatin molecule.[274]



Mechanism of Coagulation and Flocculation

It was concluded by Harold S. Olcott and Heinz Fraenkel-Conrat[275] that

The affinity of proteins for water, as measured in the present study, appears to be associated primarily with the polar groups of the amino acid side chains. When these are blocked by the introduction of hydrophobic groups, the water absorption is considerably decreased. It was shown elsewhere that phenyl isocyanate reacts with most of the amino, guanidyl, imidazole, amide, carboxyl, and phenolic groups of proteins under the conditions described.[276] It is therefore not surprising that this reagent can be used successfully to reduce the water absorption of all the proteins tested.

Phthalic anhydride treatment greatly reduced the number of basic but increased the acid groups of proteins; yet with some proteins this reagent gave derivatives of similar water absorption to those of the phenyl isocyanate and benzoyl drivatives, which are low in acid groups. Although it is appreciated that the carboxyl groups of phthalic acid may not correspond in their behavior to those of proteins, nevertheless this observation suggests that carboxyl groups do not play so important a role in determining the hydrophilic tendency of proteins as do their basic groups.

Flocculation of silver halide emulsions with polymers and polyelectrolytes is not thought to depend upon electric charge but on a different common mechanism. A. M. Kragh[277] concluded that "flocculation occurs when the surface of the suspended particles is only partially covered with adsorbed molecules, so that molecules attached by only a few segments to one particle can interact with the free remaining surface of other particles and form molecular bridges between them."

It has been proposed[278] that a distinction be made between coagulation and flocculation. Coagulation occurs when colloidal particles are united, such as by a reduction of the repulsion of electrical double layers. Flocculation involves high-molecular-weight compounds that bridge and unite the particles of a dispersion. The flocculated material is generally larger in volume than the coagulated sediment.

INCREASING THE SENSITIVITY OF THE SILVER HALIDE GRAINS

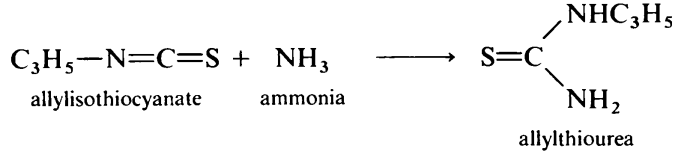
The growth of the silver halide microcrystals during the initial precipitation and the continued growth during the physical ripening produces enlarged crystals of increased sensitivity to light.[279–283] Growth is both by a dissolution of small grains which then deposit on the larger grains (Ostwald ripening)[284] and a coalescence of crystals.[285,286] Compounds, such as ammonia, ethylenediamine tetraacetic acid, or various amines or quaternary compounds, may be added to accelerate grain growth.[287–288] There is a limit to grain size, however, as the developed photographic images become increasingly grainy. Light sensitivity increases proportionally to the increase in the average grain size only up to a definite grain size, after which the light sensitivity increase slows, according to the experiments of V. V. Vasil'ev.[289] But the ripened silver halide crystals are still relatively inefficient in forming latent image. When an actinic quantum of light strikes such a silver halide microcrystal, a photoelectron is ejected from a bromide ion, forming an uncharged bromine atom (called a positive hole). If the bromine atom and the electron combine again, as would be almost certain in a perfect crystal formed in inert gelatin, then the effect of the exposing light would be lost and the crystal would be insensitive. Because of the nature of their precipitation, silver halide microcrystals are not perfect in structure but contain structural imperfections that can hold or trap photoelectrons. The bromine atoms (holes) or the combination of a hole and a silver ion vacancy then can migrate to the surface of the crystal. This ability of the ripened silver halide crystal to respond to light exposure is called its primitive sensitivity.

Chemical sensitization is a part of the emulsion-making process that increases the sensitivity of the silver-halide crystals above the primitive

sensitivity by increasing the effectiveness of the trapping of photoelectrons and the positive holes.[290–292] This chemical treatment, often called second ripening or afterripening, is dependent not upon crystal growth but upon heating the emulsion in the presence of chemical ripeners. During the digestion the chemical sensitizers improve the efficiency of the surface traps so that surface latent images are formed. [293] The heating of the emulsion above the melting point of gelatin may last for minutes or hours to provide time for the chemical ripeners to act. The sensitivity of the emulsion increases to a maximum with time, at which point the digestion must be stopped, as overripening may make the silver halide crystals developable without light exposure—that is, fog formation. Although a multitude of chemical addenda are added to photographic emulsions, chemical sensitizers are essentially of three kinds: (1) sulfur, (2) reduction, or (3) gold and precious metals.

Sulfur Sensitization

The early emulsion makers found that their silver halide photographic plates varied in sensitivity depending on the particular batch of gelatin used to make the emulsion. There were active gelatins that gave higher sensitivity and restrained gelatins that lowered emulsion sensitivity. One story tells how George Eastman spent some frenzied weeks in 1881 when all the Eastman plates suddenly were reported to be extremely low in sensitivity.[294,295] The cause was found to be the use of an inactive or restrained gelatin that did not contain the sensitizing impurities of the previous supply. S. E. Sheppard[32] was the first to show that sulfur compounds in the active gelatins were the cause of the increased sensitivity of the emulsions made with the active gelatin. He found that "This sensitizing property of certain gelatins has been traced to the presence of very small traces of organic isothiocyanates (thiocarbimides) and thiocarbamides, and specifically allyl mustard oil and allyl thiourea." The effective sulfur sensitizer was believed to form by



Thiourea and its derivatives are strongly adsorbed to the surface of silver halide crystals, then decompose to form sulfide.[296–299] Sheppard also claimed sodium thiosulfate as a sulfur sensitizer in his 1926 U. S. patent.[34]

Sodium thiosulfate is now known to act as does the natural sensitizer of active gelatin. H. W. Wood[37,300] has concluded that isothiocyanates and thioureas do not occur naturally in gelatin but that thiosulfate is the sensitizer

present. This compound may have been formed by the degradation of a sulfur-containing amino acid during the treatment of the collagen to produce the gelatin.[35,301] There is general agreement that thiosulfate is the sulfur sensitizer in gelatin, and this compound is often used with inert gelatins for sulfur sensitizing of silver halide emulsions. Careful control of the alkalinity and silver-ion concentration of the emulsion during sulfur sensitization will substantially increase the sensitivity and gradation of the emulsion coating.

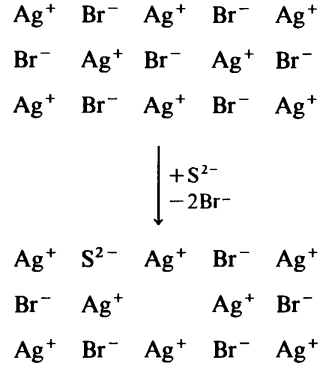
The thiosulfate ion is believed to be adsorbed on the surface of the silver halide:[302–304]

$$\underset{\text{thiosulfate ion}}{S_2O_3^{2-}} + \underset{\text{silver bromide}}{2AgBr} \rightleftharpoons \underset{\text{silver thiosulfate}}{Ag_2S_2O_3} + \underset{\text{bromide ions}}{2Br^-}$$

The thiosulfate ion is weakly adsorbed to the surface of the silver bromide crystals, but during the heated conditions of ripening and in an alkaline environment some of the silver thiosulfate decomposes. Silver sulfide is formed at discrete locations on the surface of the crystal:

$$\underset{\text{silver thiosulfate}}{Ag_2S_2O_3} + \underset{\text{hydroxyl ion}}{OH^-} \longrightarrow \underset{\text{silver sulfide}}{Ag_2S\downarrow} + \underset{\text{hydrosulfate ion}}{HSO_4^-}$$

Sulfur sensitization of crystal surface may be represented as follows (J. Pouradier, *Photographic Theory*, A. Hautot, Editor, Focal Press, London, 1963, p. 122): (By permission of Focal Press, London)



Most investigators agree that sulfur sensitization results in the formation of silver sulfide on the surface of the silver halide crystals, but there is no agreement as to the exact function of the silver sulfide.[305–309] The early Gurney-Mott theory of latent image formation proposed that the silver

sulfide acted as a trap for electrons; the more recent Mitchell theory suggested that the silver sulfide is part of the silver halide surface and acts to trap the released bromine or positive holes from light exposure.[310] The silver ions associated with the silver sulfide would act as electron traps; that is, the free silver ions could combine with electrons in the formation of the latent image. A layer of silver sulfide was found by W. West and V. I. Saunders[311] to trap both electrons and holes. This interpretation has been questioned by K. V. Chibisov,[312,313] who has suggested that the silver sulfide acts only as a catalyst for the reduction of silver ions. In this case metallic silver specks would be the effective substance. Many investigators, however, have been able to distinguish between sulfur sensitization and the effect of metallic silver centers, and they vehemently question the fundamental accuracy of the Chibisov concept.

The obvious commercial significance of sulfur sensitization has triggered an immense amount of research on the decomposition of sulfur-containing compounds on silver halide surfaces.[314–321] Some investigators state that the silver sulfide exists as islands of monomolecular thickness at the sensitivity centers of the crystals. Others have proposed more massive clusters of silver sulfide. At the moment, most could agree with the statement of Fritz Dersch:[322]

> In summary, it can be postulated that the end product of sulfur sensitization is Ag_2S, that it is intimately connected with the silver halide crystal, and performs such functions as to provide deeper electron traps than silver, to capture positive holes, i.e., react with halogen and stabilize the silver nuclei on the crystal surface. A still better understanding of the mechanism of these functions and their interrelation is desirable.

Reduction Sensitization

As early as 1927 Walter Clark[323] concluded that metallic silver as well as silver sulfide was present in unexposed silver halide crystals of enhanced sensitivity. Sodium sulfite, a reducing agent, was mentioned by B. H. Carroll and D. Hubbard[324] as a sensitizer for silver bromide. Active photographic gelatin is known to contain reducing substances, such as aldehydes, reductones, sugar, and sulfite.[325] Reduction sensitizing was the name given by W. G. Lowe, J. E. Jones, and H. E. Roberts[326] to the formation of silver atoms that increased the emulsion sensitivity. The silver atoms may be formed by reducing agents present even in inert gelatin or by the addition of a reducing compound, such as stannous chloride, to the emulsion during the chemical ripening process.

Photographic emulsions were chemically sensitized in the absence of sulfur sensitizers by heating the emulsion with an excess of silver ions. This

treatment was called silver digestion by H. W. Wood,[327–329] who inferred that silver in some form was introduced into the grains. But the exact nature of the silver is in question. Tadaaki Tani[330] found that the silver specks were electrically neutral and attracted positive holes. H. E. Spencer[331] contended that the charge on the silver speck was unlikely to be neutral but is either positive or negative. Adsorption of a bromide ion would charge the center negatively; adsorption of a silver ion among the silver atoms would make the sensitivity center positively charged. The more common negative centers would trap holes (bromine) and the positive centers would trap electrons. Reduction sensitizing is more efficient when used with sulfur sensitization.

Gold Sensitization

As the result of publication of captured documents after World War II it was learned that the great increase in emulsion technology that occurred just before the war was due to the use of certain complex gold salts as chemical sensitizers. The gold sensitizers allowed a two- to fourfold increase in the sensitivity of emulsions without increases in graininess. Fine-grain emulsions of relatively high speed became available, especially for use in 35mm cameras. R. Koslowsky of the Agfa Film Plant was the first to demonstrate that substantial increases in sensitivity could be achieved by the addition of ammonium or potassium aurous thiocyanates during the chemical sensitization treatment.[332,333] Gold sensitization alone is of limited value, but it is very effective when combined with sulfur sensitization. Koslowsky found that the gold solution could be added just before the emulsion was coated. But the exact conditions of the use of gold compounds are critical if the formation of fogged silver halide grains is to be avoided.

According to F. W. H. Mueller[334] Koslowsky "assumed that the silver halide dissolving action of excess alkali thiocyanate and thiosulfate made available silver nuclei (subsurface?) which were formed during the ripening process and which were then partially replaced by gold." Trivalent or univalent gold salts could react with gelatin to give gold gelatinates, according to a proposal by A. Steigmann.[335] In the presence of adsorbed bromide ions on the grain surface, the gold would be reduced to gold atoms. The presence of ammonium gold thiocyanate in a gold-iridium Abney emulsion gave a 16- to 32-fold increase of speed, depending on the gelatin.[336] Many investigations of gold sensitization have been carried out by P. A. Faelens.[337–342] He investigated gold, palladium, and platinum sensitization and found the gold salts to be the most effective but concluded that metal sensitization is only partly explained by the mechanism postulated by Koslowsky and Mueller. Fritz Dersch[322] concluded, "The increased sensitivity of a gold-sensitized emulsion may be due to an increase in size of the

sensitivity specks or more likely to a stabilization of the latent image speck, AgAu being more stable than Ag_2. No clarity exists on the question whether in this mechanism gold atoms are added to existing silver or whether part of the silver is replaced by gold." The gold may be in the form of a sulfide, but no analytical technique is yet sensitive enough to detect this.

Combined Chemical Sensitization

Active photographic gelatins may contain natural sulfur sensitizers as well as reducing agents. An emulsion made in such a gelatin would be subjected to combined sulfur and reduction sensitization during the heating of the emulsion. Sulfur and reduction sensitizing are additive in effect.[343] Silver sulfide formed under these conditions probably would contain more silver than would be present from sulfur sensitization alone, and this may make the silver halide with the combined sensitization more sensitive to light than with sulfur sensitization alone. Sulfur, reduction, and gold sensitization may be used in combined forms.

Although much work has already been reported, the mechanism of combined sensitization is still to be elucidated. H. E. Spencer and R. E. Atwell[344] found "reduction-sensitizer centers trap holes, silver sulfide centers trap electrons but not holes." But there is still doubt about the mechanism of combined sensitization. The sensitivity specks and the latent images of a gold-sensitized emulsion are known to be more stable than those in sulfur- or reduction-sensitized emulsions. Gold sulfide or silver-gold sulfide (AgAuS) may be formed during sensitization, and these compounds may account for the enhancement of sensitivity when gold sensitization is used. However, the effect of gold appears to be based on more than one mechanism of action. The study of combined chemical sensitizations is of great interest because it is the basis of modern high-speed photographic materials.

Spectral Sensitization

Only light that can be absorbed can be effective in the formation of a latent image. Silver chloride is white, absorbing light only near the ultraviolet end of the spectrum. Silver bromide is a pale yellow color and is sensitive only to the violet and blue light as well as the ultraviolet. Silver iodide is a deeper yellow. The addition of small quantities of iodide to silver bromide emulsions results in only a slight increase in the extent of light absorption of the emulsion. The lower-energy light reflected from green, yellow, orange, and red objects has very little or no effect on a silver halide emulsion layer. A print made from a developed negative would render any of these colored objects essentially as though they were black. (See Figure 8.)

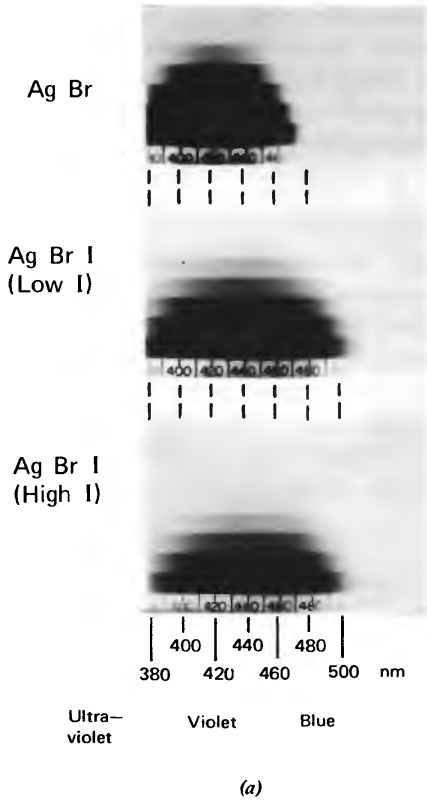
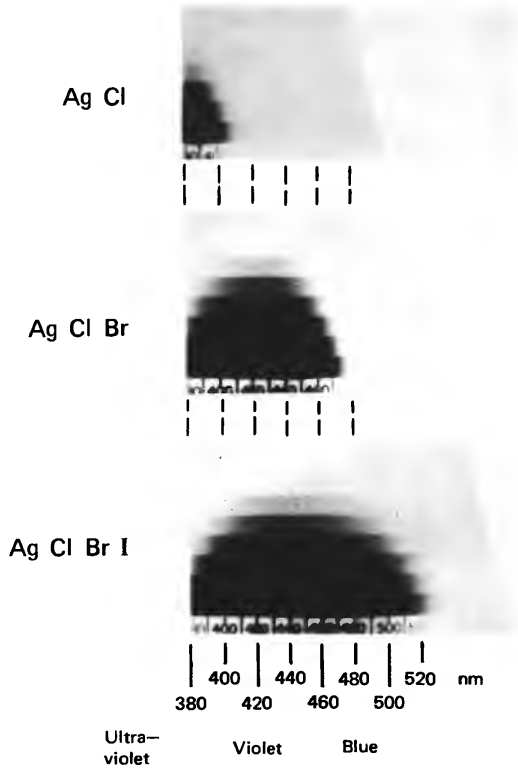


Figure 8. Spectral sensitivities of mixed silver halides. (Paul B. Gilman, Jr., Eastman Kodak Company)

A chance observation by Hermann Vogel in 1873 provided the basis for correcting the color blindness of silver halide grains.[345–349] While photographing the spectrum with dry collodion plates, whose overcoating had been secretly tinted by the manufacturer with a yellow dye to reduce halation, Vogel noticed that such plates showed a maximum of sensitivity to green light. When Vogel learned that the emulsion overcoat contained a yellow dye, he correctly surmised that the dye might be aurine, a yellow-brown compound whose sodium salt in solution was the magenta-colored dye called coralline. Although Vogel confirmed his findings by experimental results, his discovery was rejected by such well-known photographic scientists as D. van Monckhoven[350] and M. Carey Lea.[351–352] The spectral sensitization of gelatin dry plates did prove to be especially difficult. In 1876 the first practical sensitizing dye (eosin) was found by J. Waterhouse.[353] Later, the dye erythrosin was used in commercial products. But these early dyes extended the spectral sensitivity of the color-blind silver halide only into the green region



(b)

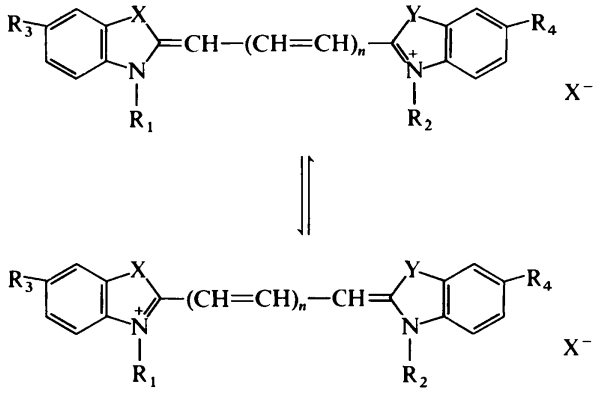
Figure 8. (*continued*)

of the spectrum. This type of sensitization, called orthochromatic, was an improvement, but red and orange objects were still reproduced abnormally dark in photographic prints. Panchromatic sensitization eventually produced a more realistic rendition of red-colored subjects. (See Figure 9.)

The early uses of sensitizing dyes mark the beginning of the search for better dyestuffs and a better understanding of how they work. Present-day spectral sensitizing uses dyes not of the early types but of the polymethine type. Cyanine dyes have a complicated structure involving an odd-numbered chain of carbon atoms, the ends of the chain usually possessing atoms in ring structures. The true cyanine dyes have the odd-numbered carbon chain attached at the ends to nitrogen atoms that are part of ring structures. One nitrogen is positively charged. The bonds joining the carbon and the nitrogen atoms in the chain and rings alternate in being singly and double bonded.

For maximum dye effect all these bonds must lie in a single plane. Many, many variations of the cyanine dye molecule have been proposed. Related dyes, such as the merocyanines, have an even-numbered carbon chain connected to rings at each end, one ring containing a nitrogen, the other usually a oxygen or sulfur.

The general formula for cyanine dyes may be written as follows:



where $n = 0, 1, 2, \ldots$

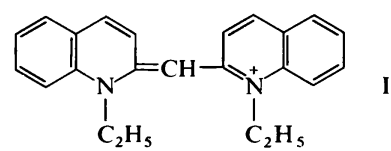
$$X, Y = -CH{=}CH-, O, S, Se, \rangle N-CH_3, \ldots$$

$$R_1, R_2 = CH_3-, C_2H_5-, \ldots$$

$$R_3, R_4 = H, CH_3-, C_2H_5-, CH_3O-, Cl-, \ldots$$

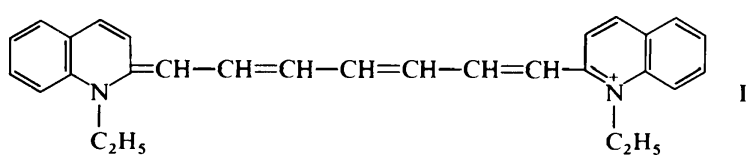
$$X^- = Cl^-, Br^-, I^-.$$

Examples: $n = 0$:



1,1′-diethyl-2,2′-cyanine iodide

$n = 3$:



1,1′-diethyl-2,2′-tricarbocyanine iodide

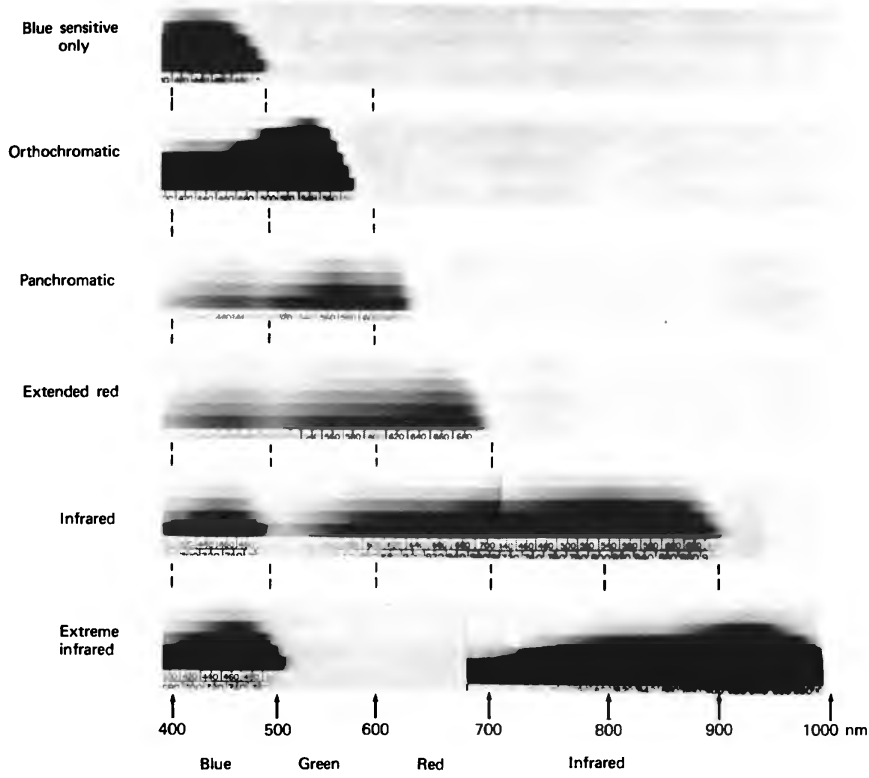


Figure 9. Spectrally sensitized silver halide emulsions. (Paul B. Gilman, Jr., Eastman Kodak Company)

The length of the carbon chain is an important factor, since the spectral absorption of light increases to longer wavelengths as the chain lengthens. But the nature of the ring structures at the ends of the chain also plays an important role in the light absorption of the dye. (See Table 3.)

This type of molecular structure for a sensitizing dye is necessary, as the dye must be able to exist in two different energy states: a normal or ground state and an excited state after the absorption of light energy. This electronic excitation produces an exciton—a quantum of electronic excitation energy (electrically neutral) that can move through the periodic arrangement of dye molecules. The dye molecule requires atoms such as nitrogen and oxygen that can exist in different states, and these atoms must be joined by a chain of carbon atoms that can transfer or resonate energy through the molecule. The electronic condition provided by the alternate single and double bonding of the chain provides a means to transfer the energy rapidly and easily. In a

Table 3. Spectral Sensitization by Cyanine Dyes

Class	Heterocyclic Ring	Sensitization Region	Absorption Maximum (nm)
Pentacarbocyanine	Quinoline	Infrared	1080
Tetracarbocyanine	Quinoline	Infrared	940
Tricarbocyanine	Quinoline	Infrared	800
Dicarbocyanine	Quinoline	Infrared	710
Carbocyanine	Quinoline	Red	610
Benzothiacarbocyanine	β-Naphthiazole	Orange-red	600
Selenacarbocyanine	Benzoselenazole	Orange	570
Thiacarbocyanine	Benzothiazole	Yellow	560
Indocarbocyanine	Indoline	Yellow-green	550
Benzimidocarbocyanine	Benzimidazole	Green	500
Oxacarbocyanine	Benzoxazole	Blue-green	485
Thiazolinocarbocyanine	Thiazoline	Blue	440

cyanine dye containing a nitrogen atom in a ring at each end of the chain, one nitrogen is electron acttracting, the other is electron donating. However, the nitrogens can rapidly exchange their roles. The dye molecule thus exists in an intermediate state of shifting electronic character, a state capable of excitation when light energy is absorbed.

After the chemical sensitization of the silver halide emulsion, a very low concentration of the dye is added from water solution, if the dye is water soluble, but more probably from a water-miscible solvent, such as alcohol or amine, as many dyes are not water soluble. The effect of the dye depends on the composition of the silver halide grains, the presence of compounds on the grain surface, and the concentration of the silver and halide ions. The concentration of the absorbed dye on the surface of the grain strongly influences the nature of the light absorption.

At very low concentrations dye molecules are adsorbed singly to the grain surface, the molecules probably lying flat on the surface. The light absorption of the dye is essentially that of the dye in solution. This type of absorption is called molecular or M-band. At higher dye concentrations the dye molecules aggregate together and absorb light at a shorter wavelength than the M-band. This shorter wavelength absorption is referred to as H-band. As the dye concentration of certain dyes is increased, a narrow increase in light absorption of great intensity occurs at wavelengths longer than the molecular absorption. This longer-wavelength absorption is called J-band, after E. E. Jelley,[354,355] who discovered it.

The very strong absorption at longer wavelengths of J-band dyes has immense practical value in the sensitization of modern panchromatic and color films. Some dyes may exhibit this property both in the solution and after adsorption to the surface of the grains. In either case, at high dye concentrations the individual molecule does not exist but the dye molecules cling together to form an ordered aggregate. The minimum number of molecules in an effective aggregate has been said to be three, but at higher concentrations of the dye many hundreds may be linked together, so that the individual molecules must be of a compact form that lies in one plane only. This aggregation of molecules was first though to be absorbed so that the molecules are edge-on, parallel with each other, and tilted about 35 deg from the vertical, much like a row of books tilting on a bookshelf that is not completely filled. Current thought pictures J-aggregates as ladder or staircase structures, or overlapping like bricks in a wall. (See Figure 10.)

When light strikes a dye molecule in aggregated form, it has been suggested that the energy of the light excites the dye molecule, creating an exciton that moves freely throughout the molecule. This exciton can transfer an electron to the silver halide grain, leaving behind a positively charged dye molecule. Latent image is then formed in the crystal in exactly the same manner as when actinic light strikes it. Light absorbed by the dye on the grain surface results in spectral sensitization of regions beyond the natural absorption of the silver halide. Almost all sensitizing dyes cause a speed decrease in the region of natural silver halide sensitivity. To secure adequate rendition of all colors of light—that is, panchromatic sensitivity—highly efficient dyes must be used to compensate for this desensitizing tendency of the sensitizers.

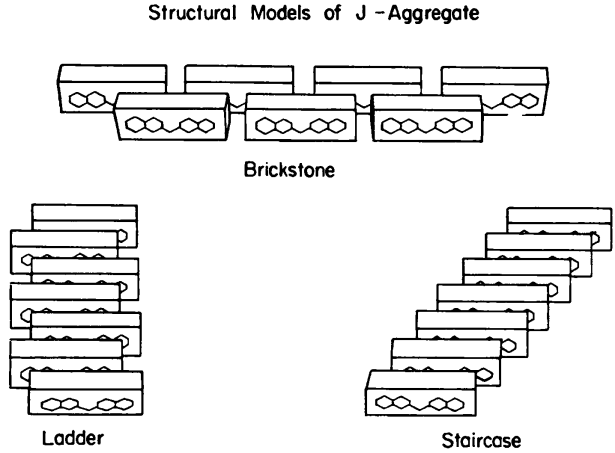


Figure 10. Structural models of J-aggregates. [V. Czikkely, H. D. Försterling, and H. Kuhn, *Chem. Phys. Letters*, 6: 11 (1970)]

Besides affecting the sensitivity to light, a sensitizing dye often produces a higher contrast in the sensitized region than in the region of natural sensitivity of the silver halide.

A high state of dye efficiency is needed to compensate for any desensitization of the dye. J-band dyes, those that exist in aggregated form at suitable concentrations, have high absorption for light energy but tend to dissipate some of the absorbed energy before transfer to the silver halide grain. This lowers the efficiency of latent image yield. In the large J-band aggregates of hundreds of molecules the energy is transferred readily from one molecule to the next. This action may be repeated many times at the expense of an energy loss. The presence of another molecule, not necessarily a sensitizing dye itself, in the J-band aggregate has been found to greatly increase the energy transfer from dye to silver halide. Supersensitization, as this technique is called, was used in practice long before the mechanism was understood. The supersensitizing molecule is now believed to provide a perturbation in the wandering of the electronic energy from dye molecule to dye molecule, slowing the energy movement so that the transfer is made more easily to the silver halide. A complete review of the mechanisms of supersensitization has been published by P. B. Gilman, Jr.[356]

Supersensitizers are used in very small concentrations (about one-tenth that of the sensitizing dye) to insure a high efficiency of energy transfer to the silver halide. Some nonplanar dyes can produce the opposite of this effect. This action is called antisensitizing. The antisensitizer captures the energy from the dye aggregate and dissipates the energy as heat. The energy is thus prevented from ever reaching the grain to produce latent image. (See Figure 11.)

The previous simplified discussion is based on many of the concepts put forth by B. H. Carroll and W. West.[357] The actual mechanism of spectral sensitization is based on complex energy and electronic transfer that is beyond the scope of this book. In recent years investigators of spectral sensitizers have gained new knowledge on the mechanism of dye interactions with the silver halide crystal. R. W. Berriman and P. B. Gilman, Jr.,[358,359] found that all dyes with a potential more negative than a certain limiting value acted as a spectral sensitizer; all dyes less negative than that value were desensitizers. It was concluded that sensitizers act as electron donors, whereas desensitizers act as electron traps. (See Figure 12.)

Tadaaki Tani,[360] as a result of an extensive study of the spectral sensitizing behavior of dye in silver bromide emulsions, has formulated a modified electron-transfer mechanism for spectral sensitization, based on his view that both sensitizing and desensitizing dyes in their excited states can transfer electrons and positive holes to silver halide grains of the emulsion. Tani states, "The electrons injected from excited dyes into silver bromide bring

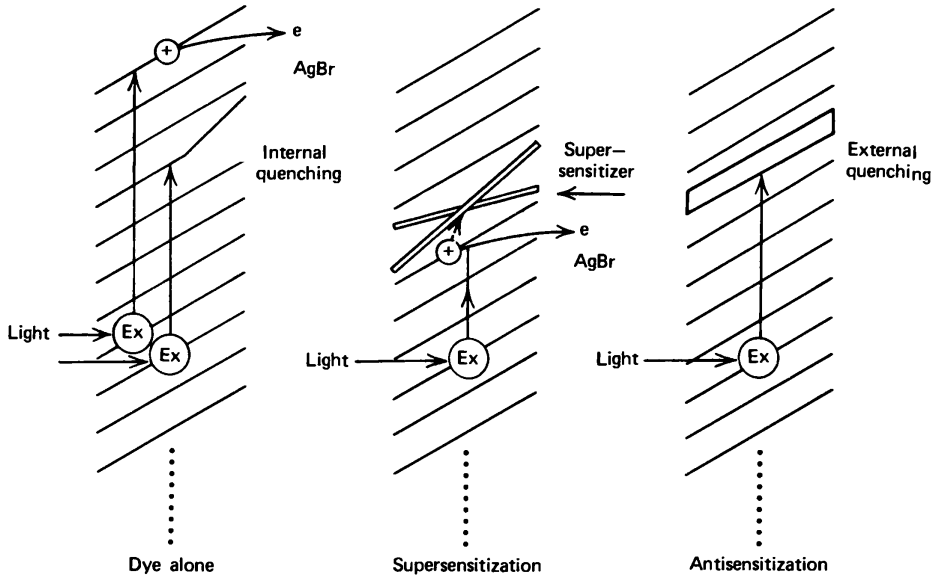


Figure 11. Supersensitization and antisensitization by exciton trapping. Excitons (Ex), generated by the absorption of light, travel through the aggregated dye layer until (1) an electron (e) can be transferred to the silver halide or (2) trapped and quenched. The supersensitizer helps the electron transfer occur before internal quenching degrades the energy of the exciton. An impurity molecule acting as an antisensitizer serves as an energy-degrading exciton trap. [Adapted from W. West and P. B. Gilman, Jr., *Phot. Sci. and Eng.*, 13: 227 (1969)]

about the latent image formation, and the positive holes injected from excited dyes into silver bromide take part in the recombination with the injected electrons and the destruction of the latent images formed by the injected electrons. When the activity of the injected electrons overcomes that of the injected positive holes, spectral sensitization can be observed."

These, however, are not the only concepts of spectral sensitization. One can certainly agree with Bill West,[361] who has devoted a working lifetime to the subject, when he concludes,

So, a century after Vogel's discovery, we must still admit that the mechanism of spectral sensitization is "incompletely understood." We do not know unequivocally the mode of transfer in the sensitizing interaction in specific cases, and, in that respect, have not progressed much beyond the intuitions of 50 years ago. This does not mean that we have made no progress in understanding spectral sensitization—on the contrary, we have much firmer grasp of the general process and a fair knowledge of details not even discussed in the 1920s, when the electronic nature of the primary process began to be widely recognized.

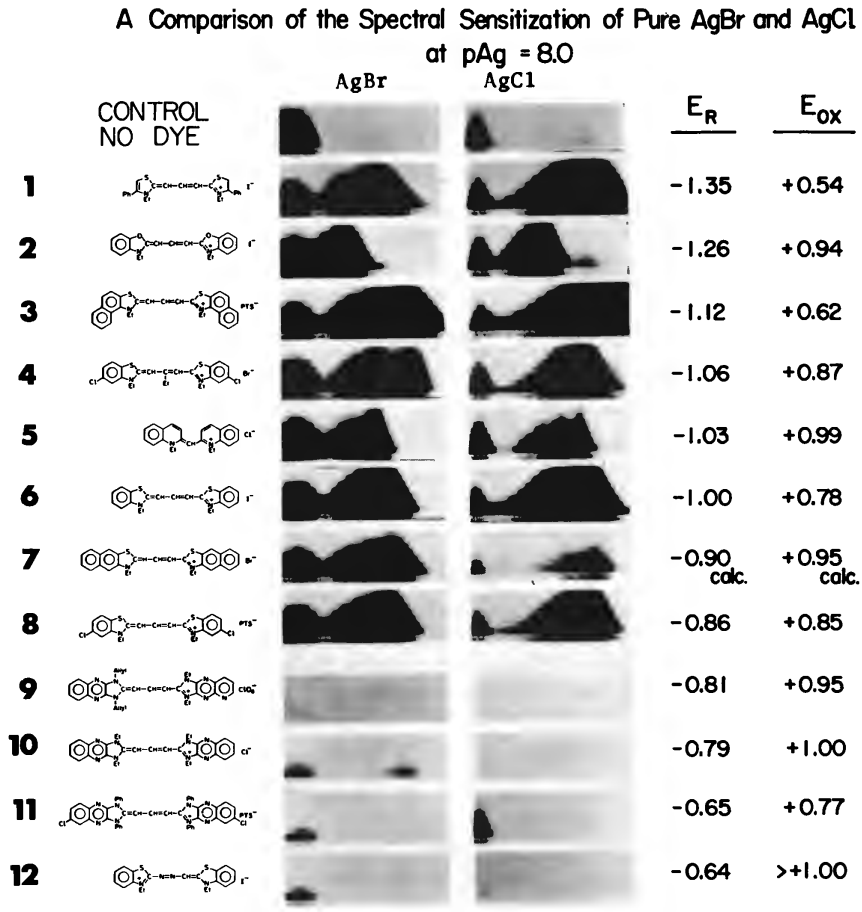


Figure 12. The potential of a dye must be above a certain limiting value before the dye will act as a spectral sensitizer. (Paul B. Gilman, Jr., Eastman Kodak Company)

PREPARATION OF THE FINISHED EMULSION FOR COATING

Restrainers

A coating of a simple unsensitized silver halide–gelatin emulsion could be useful even after 10 years of storage. But some of the early coatings of chemically sensitized silver halide–gelatin emulsions had a life of only a few months. Deterioration of the coated product resulted in a loss of emulsion sensitivity, and many grains became developable without exposure; that is, chemical fogging had occurred. In 1934 B. H. Carroll, D. Hubbard, and C. M.

Kretchman[362] showed that this fog formation would be consistent with the idea that the original chemical sensitization or ripening was continuing at a slow but persistent rate. This overipening causes a rise in the sensitivity of the coated emulsion for the first four to six months, followed by a deterioration in the sensitivity and increased chemical fogging.

Undesirable chemical sensitization must be limited both during the coating stages when the emulsion is in its liquid form and then after the emulsion has been coated. Emulsion makers originally added excess halide ions just before coating. Presumably the halide ions effectively decreased the concentration of silver ions that produce the fog centers on the grain. Gelatin with considerable restraining action was also added for this purpose. Organic restraining compounds with a known affinity for silver ions might also be added, but many of these compounds seriously decreased the emulsion sensitivity or sometimes interfered with the action of developing agents.

As a result of the U. S. and English publication of documents captured during World War II, it was learned that E. J. Birr[363–365] in 1935 had found a class of compounds that came close to the ideal for emulsion stabilization against change. These compounds were called tetrazaindenes, one compound having the name 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene. This compound still is very useful. Not only did the compound stabilize the emulsion during the coating, drying, and storage of the photographic material, but it actually produced a slight increase in emulsion sensitivity.

Other compounds are known to be emulsion stabilizers, usually carbon-containing compounds with nitrogen or sulfur present, but metal ions, such as cadmium or mercury, have also been suggested. These compounds are thought to form silver compounds that have the same or less solubility than the silver halide. These insoluble salts would lower the availability of silver ions and thus prevent further chemical ripening. This is probably true in some cases, but the true mechanism of chemical restrainers is not completely known. The action of some restrainers, such as the azaindenes, may be entirely different than that of salt-forming compounds. Thomas R. Thompson[366] has proposed that restraining compounds may prevent the growth of active or partially formed sensitivity specks. The true mechanism of emulsion stabilization will probably await a better understanding of the chemical sensitization process.

Antifoggants

A properly stabilized emulsion coating may still give rise to nonimage silver when processed in a very active or unrestrained developer. To combat fog production by these developers, antifogging compounds are often added to the emulsion. Examples are benzotriazole and similar restrainers as well as

sulfur-containing compounds not unlike those used as emulsion stabilizers. Compounds may be incorporated in the emulsion that are chemically inert until activated by the alkali of the developer at the time of processing. Isothiourea derivatives are examples of fog-inhibiting agents suitable for emulsion incorporation.[367]

Image Toners

Some developed silver images may be brownish or even greenish in tone. Compounds called toners may be added to emulsion preparations to produce a colder or blacker image after development. Again, as in the case of antifoggants, this type of added agent may be benzotriazole or a related compound. Compounds such as 3-methyl isoquinoline or quinone bisulfate have been patented for this purpose.[368] Sulfur-containing compounds are often used because, besides producing a blacker image tone, these compounds resist any change in image tone when photographic materials are heated, as might happen during ferrotyping to produce a glossy surface. Toners are thought to be adsorbed strongly to the grain and influence the form of the developed silver.

Hardening Agents

After coating, the emulsion layer is chill-set, then dried quickly. But during processing in alkaline solutions such an emulsion layer would swell enormously, possibly even leaving the film or paper base. Reticulation is the name given to the condition of a gelatin layer that has expanded and then contracted until the emulsion is cracked into a fine pattern.[369–372] Hardening agents are added to the emulsion just before coating to minimize the extent of emulsion swelling. These compounds may be chromium, zirconium, or other metal ions having two or more positive charges. But carbon-containing compounds are more commonly used. Formaldehyde has been in practical use for many years. This compound has several disadvantages, especially the tendency to promote fog during storage of the coating material. Many, many other aldehydes, dialdehydes, and related compounds have been patented for emulsion hardening. All emulsion hardeners are believed to crosslink the gelatin chains to form a less soluble combination. The metal ions such as chromium form intermolecular links between the acid groups of adjacent gelatin molecules.[116] The aldehydes link two amino groups of two different gelatin molecules. These linkages reduce the amount of liquid uptake during processing, thus keeping the swelling of the emulsion layer below any dangerous level. It has been concluded[373] that "the contribution of the crosslinks to the mechanical properties of these systems is neither the

simple provision of further junction points in the network nor the mere repression of the swelling. Rather, their function is the stabilization of the ordered structure, including collagen helix, and perhaps some orientation of the chains in the plane of the sheet at temperatures at which these features would melt out in the absence of the crosslinks."

A great number of compounds have been proposed as emulsion hardeners. Some of them have been succinctly summarized in British Patent 974,317:[374]

> Metal salts, such as chromium, aluminum and zirconium salts; aldehydes and halous aldehyde compounds, such as formaldehyde, dialdehydes and mucochloric acid: 1,2- and 1,4-diketones, such as cyclohexane-1,2,dione; quinones; chlorides of dibasic organic acids; dianhydrides of tetracarboxylic acids; compounds with several reactive vinyl groups, such as vinyl sulfones, acrylamide; compounds containing at least 2 easily splittable heterocyclic rings, examples of such rings being ethylene oxide and ethylene imine; and methane sulphonic acid esters of polyhydric alcohols. These hardening agents are compounds of low molecular weight.
>
> Some of them are photographically active and consequently cannot be considered for certain photographic emulsions. Other known compounds having a hardening action are disadvantageous in other respects. For example, metal salts increase the brittleness of the layers, dialdehydes colour the layers, and anhydrides and acid chlorides have the disadvantage of changing the pH value of the emulsion during the initial hardening. All compounds of low molecular weight have the disadvantage of not hardening specific layers, since they can penetrate through all layers. In addition hardening with the said hardening agents is not controllable since the hardening starts after drying and increases during storage. This effect is designated as post-hardening. With some photographic paper emulsions, this effect is extremely harmful, since the tone of the silver images of such papers is changed with increasing period of storage.

As indicated by the above summary, emulsion hardeners have not been entirely satisfactory. For this reason much research, as evidenced by many, many patents, has been done to secure improved gelatin hardening agents. Latent gelatin hardeners, which do not start hardening until the emulsion layer is placed in an alkaline processing bath, have been patented as hardener precursors.[375–377] Compounds containing vinyl sulfonyl groups have also been patented with claims for superior hardening, especially for color photographic materials.[378–380]

Polyethylene Oxides

R. K. Blake's discovery of the emulsion-sensitizing action of polyethylene oxide compounds in 1948 has been responsible in considerable measure for the rapid advancement of film sensitivity since World War II.[381] These long-chain, high-molecular-weight compounds may double the normal

sensitivity of high-speed bromoiodide emulsions without a serious increase in granularity. Current belief holds that these compounds are not chemical sensitizers of the type used during digestion of the emulsion but have the primary effect of accelerating development.[382] Polyethylene oxides adsorb strongly to silver halide grains and appear to facilitate the approach of negatively charged developing agents that are used in combination.

Coating Aids and Other Addition Agents

Plasticizers are often added to emulsion preparations to keep the gelatin from becoming brittle after drying on a flexible film or paper base. Ethylene glycol, glycerine, and similar humectants have been used to maintain moisture in the coated layer and avoid brittleness. Other gelatin plasticizers are often used to avoid the tackiness that humectants may produce in the coated layer.

Emulsions are coated in very thin layers, placed one upon the other. Wetting agents are needed to insure complete coverage of the film or paper base, then the spreading of the layers. Because of the low water solubility of some parts of the gelatin molecule, emulsion preparations tend to resist spreading in thin layers, producing uncoated areas (resist spots or streaks). One end of the wetting-agent molecule usually is water soluble, the other end having low water solubility. By acting in the interface between the surface and the aqueous emulsion being spread upon it, the wetting agent helps to produce even spreading of the coated layer. An extensive review of wetting agents for emulsion coating has been given by B. V. Deryagin and S. M. Levi.[383]

Saponin, a naturally occurring product, has been used for many years to coat emulsions, but many synthetic products, not unrelated to household detergents, are used commercially. Gelatin emulsion preparations using saponin or other wetting agents may froth easily, producing bubbles that would interfere with the coating process. Antifoaming agents, usually alcohols of moderate chain length, may be added to break the foam, but now emulsion preparations are often degassed through the use of sonic generators.

Coating the Emulsion

The chemical marvel that is a silver halide emulsion, chemically and spectrally sensitized, with the addition of restrainers, stabilizers, antifoggants, hardeners, coating aids, and even dyes to improve the sharpness of the processed image, may be coated by a number of different technologies. Elaboration of such techniques is not within the scope of this book. Briefly, however, the emulsion layer may be picked up by the moving base material, as by its licking the surface of the emulsion in a trough, or it may be extruded

from a slitted hopper onto the base. Most industrial photographic products are made by the hopper-fed technique, the liquid emulsion being pumped through the hopper slit as the base races past at high speed. More than one hopper, or a hopper with multiple slits, may be used for the simultaneous coating of multilayer products.

The top layer of the emulsion (the T-coat) is usually a thin layer of gelatin to protect the emulsion from abrasion. Such a gelatin layer is necessary if the product is to have a glossy finish as the result of glossing. A considerable amount of the gelatin hardener, sometimes the entire amount, is added in this top gelatin layer. The hardener diffuses to harden the other emulsion layers. Fine particles of transparent substances, such as starch or silica, may also be added to the topcoat to produce a rough surface for retouching or for better handling of prints. Polymeric substances may replace the gelatin in the top layer. Lubricants may be added to the top layer of motion picture film.

PHOTOGRAPHIC BASE MATERIALS

The base or support upon which the emulsion is coated plays an important part in determining the properties of the coated emulsion. Glass plates and paper were the early supports for camera photographic products. Glass furnishes an excellent rigid support but is heavy, bulky, and easily broken. In 1889 George Eastman's chemist, H. M. Reichenbach, mixed nitrocellulose and wood alcohol to form a flexible film that could be cast upon a smooth surface. Camphor, fusel oil, and amyl acetate were added to the casting mixture, mainly to provide tensile strength. This composition was patented[384] without delay, but in 1898 H. Goodwin was awarded a patent as a prior inventor of a flexible film material, based on Goodwin's 1887 patent application.[385]

The original flexible film base, cellulose nitrate, continued to be used until about 1940. But cellulose nitrate is highly flammable, supplying its own oxygen as it burns; thus, once it catches fire, it is very difficult to extinguish. Several major conflagrations swept installations where large amounts of film were stored or used. Such fires emphasized the need for a safety film base. The cellulose used to make film base was then modified by treatment with acetic acid to give cellulose acetate.[386] The properties of the base depend upon how much acetic acid is incorporated. Cellulose triacetate, the film base still in some use today, contains about 43% attached acetic groups. The film base is cast upon a smooth surface, usually continuously upon a rotating wheel, and the solvents are driven off by heating. Plasticizers, such as tri-*m*-cresyl phosphate, are included in the film base to keep the film flexible and free from brittleness.

Cellulose triacetate is indeed a safety film, as it is difficult to keep burning once ignited. But it suffers from some disadvantages. Its mechanical strength is less than desired. It takes up a considerable quantity of water during wet processing, then does not shrink to exactly its former size after it is dried. Many other modifications of cellulose have been tried, but none overcome completely the original deficiencies.

The reaction of the dimethyl ester of terephthalic acid and ethylene glycol when heated under a vacuum in the presence of a catalyst produces a polymer. The molten polymer is extruded from a slit, then the sheet is stretched both sideways and lengthways.[387] This stretching technique orients the molecules to produce a thin, tough transparent film of low water take-up. The film is not a fire hazard. This polyester film is the type that is available in Du Pont's Cronar and Kodak's Estar products.

Aqueous emulsions cannot be coated directly upon cellulose acetate or polyester film bases because the emulsion layer will not adhere. The film bases must be first treated or prepared to accept the emulsion. Thin layers, called subbing, are added to the film base to give the emulsion something to cling to. With cellulose triacetate the base may be etched with solvents so that subbing is fairly easy to accomplish. But the inertness of the polyester film has made subbing much more difficult. Multiple thin layers have to be built up, the character of each polymeric layer slowly changing from that of the base to a layer that will allow an aqueous emulsion to spread and adhere.

Film base may be subbed on both sides, one side to receive the emulsion, the other side for a backing layer. The backing layer usually contains gelatin or a suitable substitute that is designed to counteract the curling action of the emulsion layer. In the backing layer may be a dye or pigment to absorb the light from being reflected through the emulsion a second time. Because it minimizes this halation effect, the backing layer is often called the antihalation backing. Sometimes the function of the backing layer is incorporated into the film base itself, as in the gray base cellulose triacetate materials. Carbon dispersions, black resins, or suitable dyes are used to absorb the light and prevent image spreading. Backing dyes must be easily removed from the backing layer during processing. Sometimes negatives produced from aged film may retain a pink or purple dye tint, especially when processed in dilute, weakly alkaline developers. Both the dye in the backing layer and the ingredients of the subbing layer must be as chemically inert as possible, as both contact the emulsion layer during storage of roll, sheet, and 35mm films. Incorporation of the antihalation dye beneath or within the emulsion layer is possible, but undesirable interactions with the silver halide must be avoided.

Photographic paper base is made from cellulose fibers derived from wood.[388] During manufacture every precaution is taken to insure that the

paper will have maximum strength. Melamine resins or other agents are usually added to improve the wet strength of the paper even further. Paper for photographic prints often has a surface layer to provide a smooth base for coating the emulsion as well as increasing the whiteness of the paper base. This layer is coated from a suspension of barium sulfate in a gelatin solution, usually applied in one or two layers and calendered under pressure to provide a smooth surface.[389]

The baryta layer may include a considerable number of chemical additions. One or more dyes may be used to counteract the natural yellowish tinge of paper base or the gelatin of the emulsion. Some dyes, called optical bleaches, absorb ultraviolet radiation, then fluoresce with a bluish color. This gives a print of increased effective contrast, a "whiter white," but the effect may vary with the illumination.

Photographic paper base is now often resin coated, usually with polyethylene on both surfaces to minimize absorption of processing solutions. It is difficult to make an emulsion adhere to such a water-resistant surface. One method is to use in-line electron bombardment. Apparently, the molecular structure of the polyethylene is sufficiently disrupted so that the photographic emulsion will adhere if the coating occurs shortly after the electron bombardment.[390]

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Chapter 3
The Latent Image

The structure of the latent photographic image and its origins are problems which are as old as photography itself; however, they are not yet solved.

JOHN EGGERT[126]

One day in September, 1840, W. H. Fox Talbot had been exposing various sensitized papers in the camera obscura, a dark box whose small aperture projected images to the rear of the box. Exposure times were normally very long, as the paper had to be exposed to light until the image formed in the camera. But Talbot gave relatively short exposures, as he wished to find which of his papers was the most sensitive to light. One of the exposed papers had been given too short an exposure. When it was examined by candlelight, the paper possessed no visible image. This paper was left on a darkroom table. Some time later Talbot was amazed to see that a distinct picture had formed on the paper.

Fox Talbot concluded that the picture had formed itself by the spontaneous action of the ingredients in the paper. He repeated the experiment immediately. This time he watched the exposed, sensitized paper by the light of the candle. The image details appeared slowly and continued to grow until the image was fully formed. Talbot concluded that the original light exposure had formed an invisible or latent image which then continued to grow until it became visible. He had discovered the presence of latent image in exposed

photographic paper that was a forerunner of today's photographic materials.[1]

Ever since its chance discovery, the latent image has intrigued and challenged all those who are interested in the photographic mechanism. Modern photographic film, after a brief exposure, shows no detectable change, either to the human eye or to the most powerful electron microscope.[2,3] Modern analytical techniques are unable to reveal the changes that must have been caused by the exposing light. But the change is there, because when an exposed film is placed in a photographic developing solution, the light-struck parts of the emulsion layer are converted to a dark image of metallic silver. The unexposed parts remain essentially unchanged. The

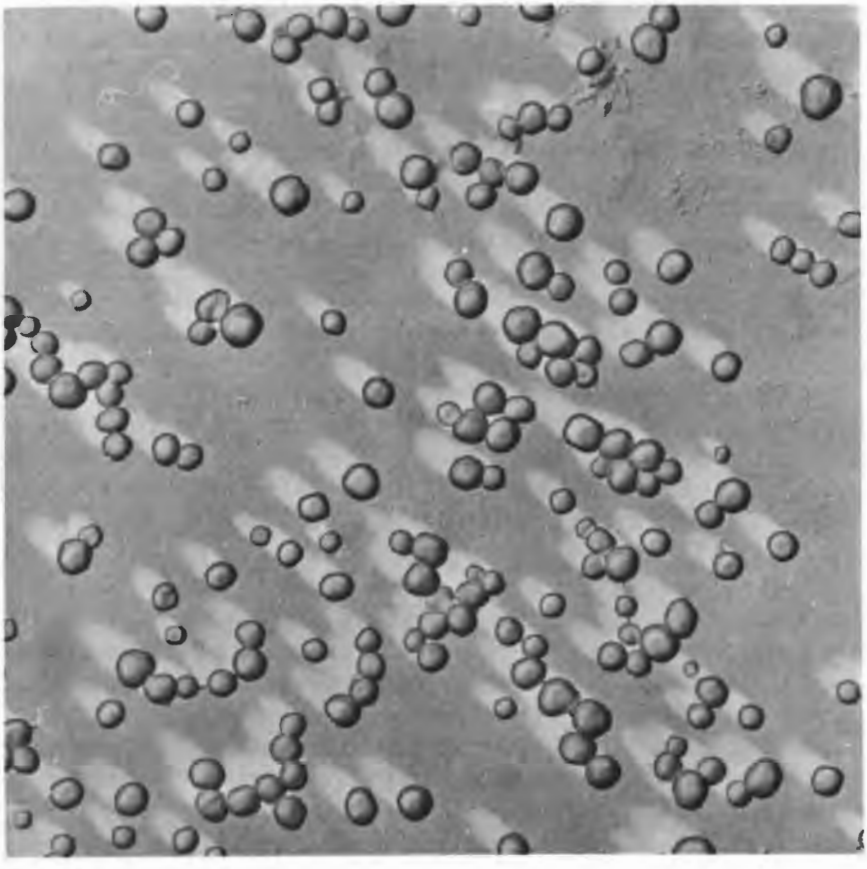

Figure 1. Silver halide grains in commercial products are often imperfect spheres. These chlorobromide grains are from a photographic paper for making color prints. (Carbon replicas, shadowed, at 12,000 ×) (Eastman Kodak Company)

photographic developer converts the latent image into a visible negative image, so called because the tones on the film are the reverse of those of the original subject.

The latent image represents a catalytic condition of the silver halide microcrystals that can be detected by the chemical action of the developer. Sometimes, instead of a developer, continued light exposure in the camera may be used to reveal the latent image.[4] But in either case the latent image has been destroyed and replaced by the visible image. Thus, any information about the invisible effect of light exposure must be indirect, making the interpretation of such studies both difficult and highly debatable.

The silver halide microcrystals of a photographic emulsion are commonly called emulsion grains, or simply grains, and the metallic filaments of the developed silver image are called developed grains or silver grains. Often, however, the term grain is used to describe either the emulsion microcrystal or the silver filaments produced from it. This may lead to some confusion, but just which grain is intended can usually be derived from the context.

The latent image within the silver halide grain is invisible, but the grain itself can be seen and studied, not with the eye but with optical or electronic equipment. In an ordinary photographic emulsion there are, according to J. H. Webb,[5] approximately ten billion grains per square centimeter of surface area. The average size of the grains is about 0.1 square micron for low-speed, positive films and about 1 square micron for modern high-speed negative films. The grains of commercial emulsions may be of different shapes but are often imperfect spheres. An average grain of a coarse-grained emulsion is estimated to contain ten billion pairs of silver and bromide ions. (See Figure 1.)

THE EFFECTS OF LIGHT EXPOSURE

Although knowledge of the darkening of silver nitrate by light has been attributed to the ancient Egyptians, it was not until 1727 that Johann Heinrich Schulze observed that chalk saturated with nitric acid, containing some silver impurities, was rapidly darkened by the sun. He correctly attributed the light sensitivity to the silver nitrate rather than the chalk and carried out simple experiments by placing thread, wire, or cut-out letters or words on the glass container of the chalk and silver nitrate mixture. The parts of the glass not shielded from the sun darkened, leaving the shielded parts unchanged. Schulze, however, does not appear to have considered a practical use for his observation.[6]

Fifty years later, in 1777, Charles William Scheele made the first scientific study of a silver salt.[7,8] He allowed the sun to blacken silver chloride, then

proved that metallic silver resulted from the action of light. In another experiment he exposed silver chloride to light while the silver chloride was in distilled water. The water was poured off and silver nitrate was added, drop by drop, to the water. Silver chloride was formed. Scheele concluded correctly that chlorine gas was also liberated by the action of light upon silver chloride. Scheele had demonstrated, and later confirmed with other experiments, that the continuing action of actinic light upon silver chloride is to produce metallic silver and chlorine gas. The light exposure used by Scheele, or that required to darken a modern photographic emulsion, is many million times greater than the quantity of light needed to produce a latent image that can be developed.

Examination of silver halide after irradiation has shown that the first image is metallic silver. This print-out silver is assumed to be a continuation of the action of the light that originally produced the latent image, and the latent image itself was but a few atoms of metallic silver.[9]

The few silver atoms of the latent image cannot be detected by other than chemical amplification, but the latent image can be destroyed (bleached) by chemical reagents that convert metallic silver back to the same ionic form contained in the grain. Compounds, such as chromic acid or potassium persulfate, and halogen gases, such as bromine, effectively remove the surface latent image.[10] The action of these latent image–destroying agents also suggests that the latent image must be composed of metallic silver.

Studies of surface latent image of unsensitized silver halide grains indicate that the latent image reacts as though it were composed of finely divided silver. However, with modern gold-sensitized silver halide emulsions, the latent image is not completely destroyed by a selective bleaching agent, such as mercuric chloride. This compound bleaches silver but not gold. Gold ions are thought to be firmly bound to the surface of the grain in the emulsion. During actual exposure of the grain, some of the ions of gold are converted to atoms of gold and then built into the latent image.[11]

Although the latent image may be bleached from the surface of the silver halide grain by suitable reagents, some latent image may remain inside the grain, where it was protected from the action of the bleaching agent. This image may be revealed by use of a developer containing a solvent for silver halide, such as sodium thiosulfate.[12,13] An early attempt was made by Alfons Kempf[14] to determine how the latent image is distributed throughout the silver halide crystal after exposure to light. Many others have used various techniques to resolve this question.[15–19] The distribution of the latent image specks within the volume of the emulsion grains was studied by J. Malinowski and G. Karadjow[20] using differential development. They found that "The concentration of the specks decreases steadily and monotonously towards the interior. The product of photolysis seems to penetrate from the surface

inwards, the depth of penetration increasing with exposure." J. Malinowski[21] also reported that "The distribution of the specks among the different grains of the emulsion does not seem to be random, specks being formed preferentially in some of the grains."

THE SIZE OF THE LATENT IMAGE

The chemical and physical properties of silver halide grains yield little information concerning the size of the latent image. Each grain is known to act as a separate unit; light energy is effective only when absorbed in the grain that it strikes, and it cannot be transferred between grains. Each quantum of energy that is absorbed frees one electron within the grain. If this electron subsequently results in the forming of one atom of silver, then how many absorbed quanta—that is, how many atoms of the resulting silver —are necessary to make the most sensitive of the grains developable? This tantalizing question has stimulated investigators to measure the quanta of the exposing light and make an estimate of the minimum latent image size.[22]

A photographic emulsion layer may be exposed and developed, then all but a single layer of grains next to the base washed off. By studying the remaining grains with a technique called residual grain analysis, described by G. C. Farnell and J. B. Chanter,[23] we can relate the proportion of grains developed for each size class of grains to the number of quanta absorbed. An analysis of this information reveals that no grains are made developable by the absorption of only two quanta of light. Some grains may possibly be sensitive to three quanta. But large numbers of grains are developable after absorbing four or five quanta. Most grains would be developable after absorbing ten quanta. Other grains may require many tens of quanta before being developable. Some grains do not appear to be developable at all. The need to absorb three or four quanta would appear to make latent image formation occur in a number of repetitive steps.

Farnell and Chanter found that "If a certain exposure suffices to make developable a just detectable fraction of grains of a single size, then it must be increased by a factor of 1.0 to 2.0 log units [that is, by 10 to 100 times] in order to make all grains of that size developable." They also found a tendency that the most sensitive grains in a given size class decrease in sensitivity with increasing size. Some of the inefficiency in latent image formation may be related to the number of possible sites for latent image on the grain. If the number of sites was great, then the light energy absorbed would produce electrons that would be distributed among all the possible latent image

centers. Some of the centers on some grains might never reach a stable or developable size; thus the effect of the exposing light would be wasted.

LATENT IMAGE SITES

The early stages of development may be observed through a microscope. The early work of W. Scheffer[24,25] and Millard B. Hodgson[26] indicated that development of an exposed grain occurred at one or a very few locations on the crystal surface. Continued development then caused the entire crystal

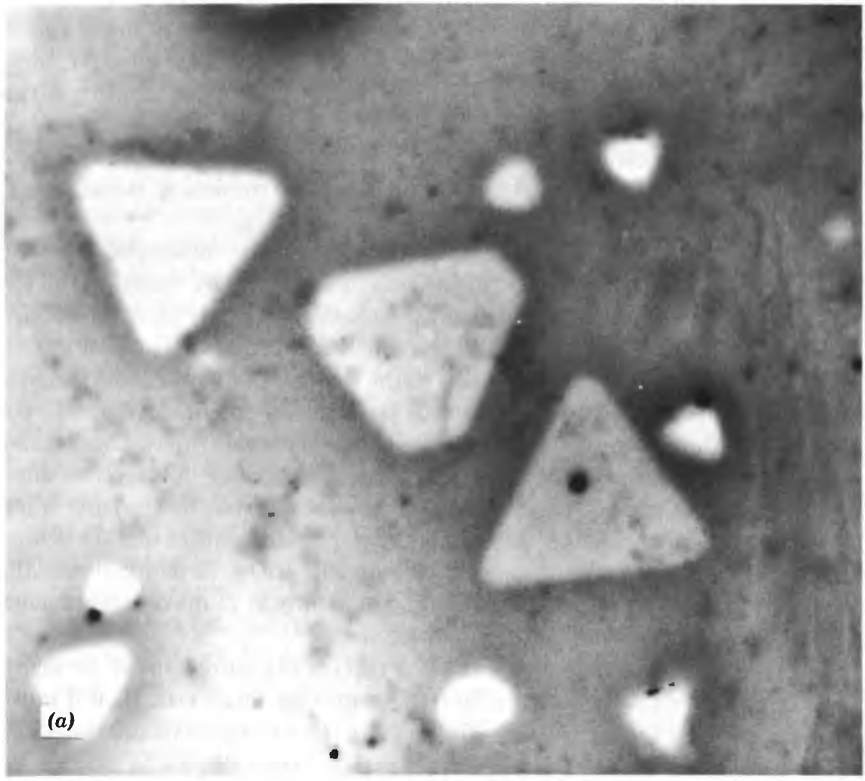

Figure 2. The location of latent image centers can be revealed by partial development. A dilute developer is used, and the action is stopped in the very early stages of reduction of the grains. After a small amount of exposure (*a*), a few grains contain a speck of silver. Continuing the exposure increases the number of specks in some grains after development. More important, however, is the increase in the number of grains with at least one speck (*b*). (John F. Hamilton, Eastman Kodak Company)

to be converted to metallic silver. The photolytic product would appear to have been concentrated at certain preferred sites on the crystal surface, even though the exposing light was evenly distributed over the surface. This product then provided the point for attack for the developing agent to reduce the entire crystal to metallic silver. It is this developable state, induced by the photo-produced product, that is called the latent image. (See Figure 2.)

A few years after Hodgson's observation in 1917 that development started at discrete points on the exposed grain, S. E. Sheppard[27–29] determined that certain sulfur compounds, often occurring naturally in gelatin, were responsible for observed increases in emulsion sensitivity. These active

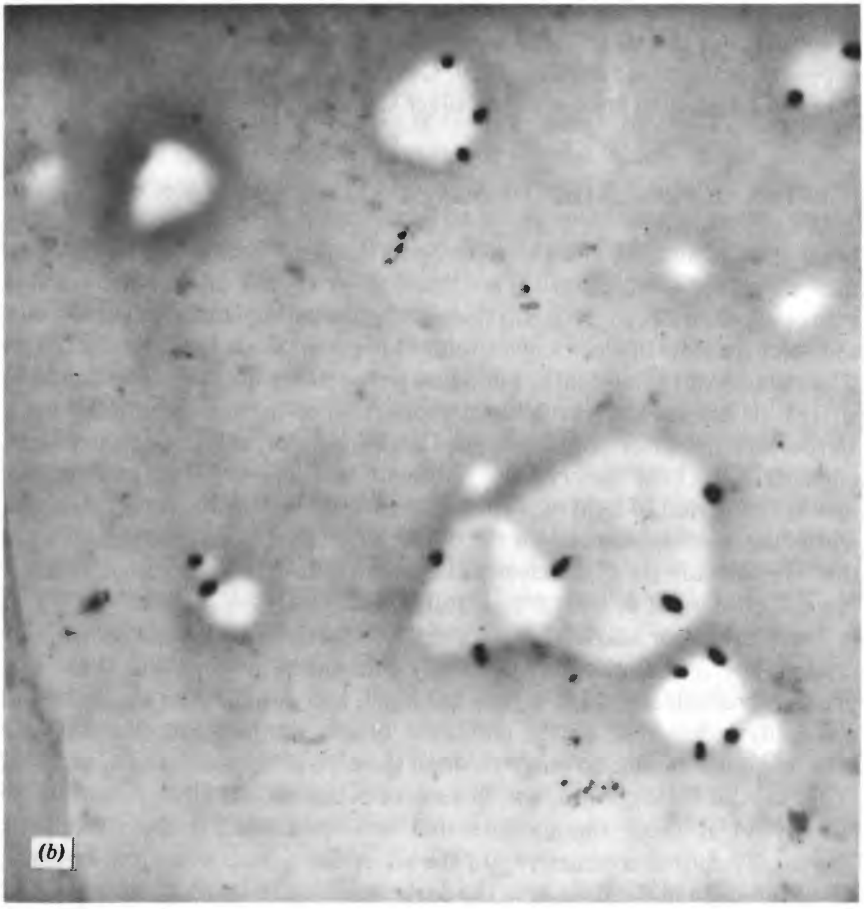

Figure 2. (*continued*)

compounds, containing the $\rangle C{=}S$ group, were present only to the extent of one part of the compound to 300,000 to 1,000,000 parts of the gelatin. Yet, this miniscule amount of the sensitizing compound was believed to combine with the silver halide at certain points on the surface of the grains. The combination of the sulfur compound and silver halide was unstable, decomposing to form silver sulfide on the grain surface. Considerable scientific study has confirmed that silver sulfide may indeed be formed during the heat treatments of the emulsion-making process.

The silver sulfide, or silver selenide or silver telluride, is not formed as an even layer over the grain surface but at a few isolated sites on the surface. Because development was observed to begin at a few discrete points on the surface of the silver halide crystal, the presence of the silver sulfide specks was assumed to be related to latent image formation. K. C. D. Hickman[30] proposed that the silver sulfide served as a halogen absorber during light exposure of the silver halide crystal. Others have suggested that photolytic silver was deposited at or near the silver sulfide on the crystal surface.[31]

ELECTRICAL PROPERTIES OF SILVER HALIDE CRYSTALS

Some insight into the effect of light upon the silver halide emulsion grains may be gained from electrical studies.[32–34] A crystal of silver bromide is made part of an electrical circuit that contains a battery and a sensitive meter to detect the flow of electrical current. No current flows through the circuit when the crystal is maintained at a low temperature in the dark; when light strikes the crystal, current flows in proportion to the intensity of the light. In the dark the silver bromide crystal is an insulator, preventing the flow of current. In the light the crystal is photoconductive, permitting current flow during the period of light exposure. The effect of light is to release electrons within the crystal, because it is the electrons, not the silver or bromide ions, that are the carriers of an electrical current at low temperature. Electrons are also efficient at normal temperatures as well.

There are other carriers of electrical conductivity in the silver bromide crystal. The crystal contains positively charged silver ions and negatively charged bromide ions. These ions are much less mobile than electrons and are easily inactivated by the condition of low temperature. Actually, the bromide ion is unable to move through the crystal because of close packing of the crystal lattice, so it is the movement of the smaller silver ions through the crystal at room temperature that is responsible for the electrolytic current. The ionic conductivity of the silver ion is not influenced by light, being the same in the light as in the dark; but the conductivity is sensitive to temperature, unlike the electronic conduction of current.

Two electrical processes occur in a silver halide crystal at normal temperatures: (1) at the instant of light exposure a quantity of electrons proportional to the intensity of the light are released; and (2) both in the light and in the dark a few interstitial silver ions move through the crystal lattice. These two actions must be fundamental to the formation of a latent image consisting of a few atoms of metallic silver.

THEORIES OF THE FORMATION OF THE LATENT IMAGE

In a square inch of a modern photographic emulsion layer there are about 100 million silver halide crystals suspended in a gelatin matrix. The average crystal contains about 100 million ion pairs; that is, 100 million silver atoms that have lost an electron and 100 million halide atoms that have gained the electron. The positively charged silver ions and the negatively charged halide ions are alternately arranged, row beside row and layer upon layer, to form each microcrystal or grain of the emulsion layer. W. F. Berg[35] has noted: "The exposure required to produce a latent image cannot possibly affect more than 10 or, at most, 100 of the ion pairs in the emulsion crystal; and, in the process of detection, both the latent image and its parent crystal are lost." This is the challenge for theorists of latent image formation—just how do those 10 to 100 ion pairs altered by light differ from the unaffected 100 million ion pairs of the same crystal?

The few observable facts often appear to be just sufficient to form a proposal for a possible mechanism for the unseeable action of light, but the facts are always insufficient to establish an incontrovertible explanation. By 1892 W. Jerome Harrison[36] in his book, *The Chemistry of Photography*, listed ten different proposals for latent image formation—five based on the chemical reactivity and five based on the physical properties of the latent image. After that time the number of theories appears to approach the number of really knowledgeable workers in the field. Such theories serve a useful purpose in guiding the experimentation of those seeking to learn more of the photographic process, but theories often do not achieve widespread acceptance, and all are subject to modification with time.

In 1925 S. E. Sheppard, A. P. H. Trivelli, and R. P. Loveland[37] proposed their concentration speck theory of latent image formation "to explain practically all the known facts." This theory, probably the first one to achieve wide acceptance, continued to be the main latent image theory for about ten years. The concentration speck theory proposed that specks of a material formed on the surface of silver halide grains during the making of a photographic emulsion. These specks resulted from the reaction of the silver halide with a substance from the gelatin, forming silver sulfide. The

specks varied in size and were scattered at random on the grain surface. The specks were involved neither in the absorption of light nor in the resulting release of electrons within the grain, nor were the specks themselves light sensitive, as had been previously postulated. The sensitizing action of the speck was due "to increasing its size by accretion of photochemically reduced silver atoms to form a nucleus large enough to induce developability."

The concentration speck theory of latent image formation gained acceptance because it did represent the best explanation of the observed facts, but it actually did not propose any mechanism for the formation of the image. In 1936 J. H. Webb,[38] using the recently gained knowledge of the electronic properties of crystalline materials, appeared to have been the first to formulate an electronic explanation of the observed facts of the concentration speck theory. The more energetic electrons of the silver halide crystal, after an absorption of light energy by the crystal, are raised to a condition where they are capable of free movement within the crystal. These freed electrons are capable of traveling a considerable distance through the crystal lattice. The electrons will then become trapped "at surface irregularities in the crystal lattice or in proximity to impurities imbedded in the crystal." Thus, Webb's theory provided the mechanism for the concentrating action of the surface specks.

But the Webb explanation was incomplete, because it failed to provide for a mechanism for the movement of silver ions through or along the surface of the crystal. A proposed mechanism for this was provided by R. W. Gurney and N. F. Mott[39] in 1938. The Gurney–Mott theory, as it is commonly called, has become the basis of our modern understanding of latent image formation. This theory has undergone slight modifications during the years of its existence, but the modern version still appears to be the best explanation of latent image formation. Other theories that have been offered appear to account for omissions in the Gurney–Mott mechanisms rather than replacing the entire theory.

The Gurney–Mott theory proposed a two-stage process, repeated a number of times, for the production of silver atoms that constitute the latent image. (See Figure 3.) An electron from a bromide ion, activated by the absorption of a light quantum, would wander in the crystal until it contacted a silver sulfide speck on the crystal surface. Because the electron could occupy a state of lower energy in the silver sulfide, the electron would be delayed or trapped in the sulfide speck. This is essentially Webb's proposal. Next, Gurney and Mott proposed that the silver sulfide speck, now negatively charged by the presence of the electron, would attract a positively charged silver ion. The most probable silver ions would be those displaced from their normal lattice positions by the movement caused by the temperature of the crystal. One of these thermally displaced silver ions would then move to the

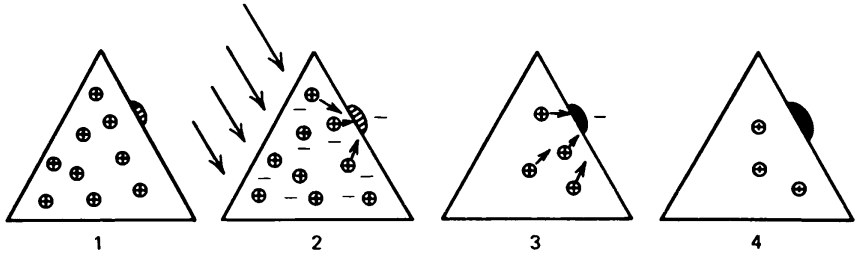

Figure 3. A representation of the Gurney–Mott mechanism of latent image formation. The large triangle represents a silver halide grain with a sensitivity speck on the surface, as shown in (1). Exposure to light (2) generates photoelectrons (—) which are trapped at the sensitivity speck. Positively charged silver ions ⊕ in the grain interior, as in (3), are attracted to the speck, forming atoms of silver by combining with the electrons there. In (4) a developable latent image has been formed by the deposition of silver atoms.

sulfide speck with the captured electron. The silver ion and the electron could combine to form an atom of metallic silver. The speck would then trap another photoelectron and the process could repeat to form the second atom of silver. In this way, the silver deposited at the speck could grow to sufficient size to provide a site for development. (See Figure 4.)

The Gurney–Mott, two-step mechanism of latent image formation provides adequate answers for many of the observed characteristics of photographic emulsions.[40] Each electron used for latent image formation is removed from a lattice bromide ion by the action of the light. A bromide atom results. This atom was presumed to diffuse to the surface of the crystal and escape into the gelatin. It would probably be formed very near the surface, because the absorption of the exposing light is mainly on the surface of the grain.

Latent image formation at low temperatures would be inefficient, because the speck could easily capture the first electron, but the low mobility of the silver ion at low temperatures would not allow a quick neutralization of the negative charge. This negative charge on the speck would then repel other electrons, and these electrons might eventually be captured by the halogen atoms in the exposed crystal. At normal temperatures but at long-time, low-light-level exposures, an insufficient supply of electrons is available at the latent image site. Latent image does not form until the electrons available exceed the normal rate of recombination of silver with the halogen atoms. At normal temperatures but high-intensity, short-time exposure a flood of electrons would be produced, but the movement of the silver ions would not be sufficiently rapid before many of the electrons were captured away from the latent image sites. In this way the latent images would contain fewer

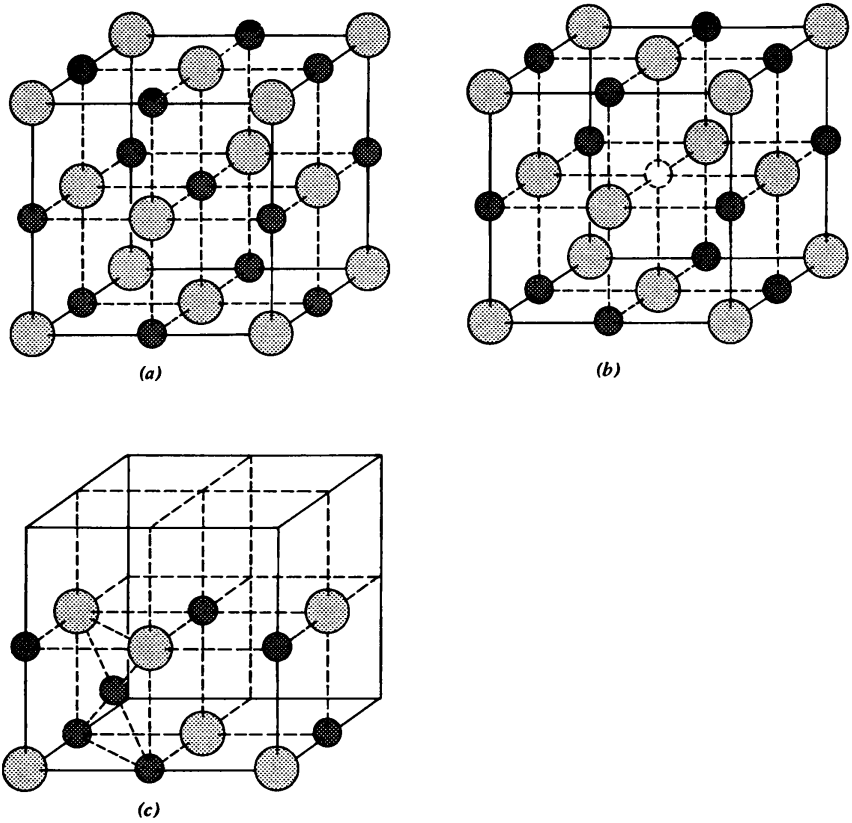

Figure 4. Diagrammatic representations of silver halide lattices, where ◌ denotes halide ions, ● denotes silver ions: (*a*) A silver halide lattice. (*b*) A silver halide lattice with a vacant silver-ion site. (*c*) A silver halide lattice showing an interstitial silver ion. (d) A silver halide lattice showing a vacant anion (bromide) site. (*e*) A silver halide lattice showing adjacent silver and halide ion vacancies. (*f*) An electron may occupy the vacancy caused by the missing halide ion, forming an F-center. (*g*) The presence of a sulfide ion, indicated with "S", effectively produces an F-center in the silver halide lattice, *Source*: W. F. Berg, *J. Phot. Sci.*, 1: 8 (1953)

atoms of silver than obtained from an intermediate light intensity at a normal exposure time. These lessened latent images at very low and very high light intensities do not produce the developed densities given by an equal exposure at intermediate conditions. The Gurney–Mott theory provides a plausible explanation for these deviations from the reciprocity law, which would predict equal densities for equal amounts of light energy.

Some objection has been made, not so much to what Gurney and Mott proposed but to what they failed to detail, concerning the mechanisms

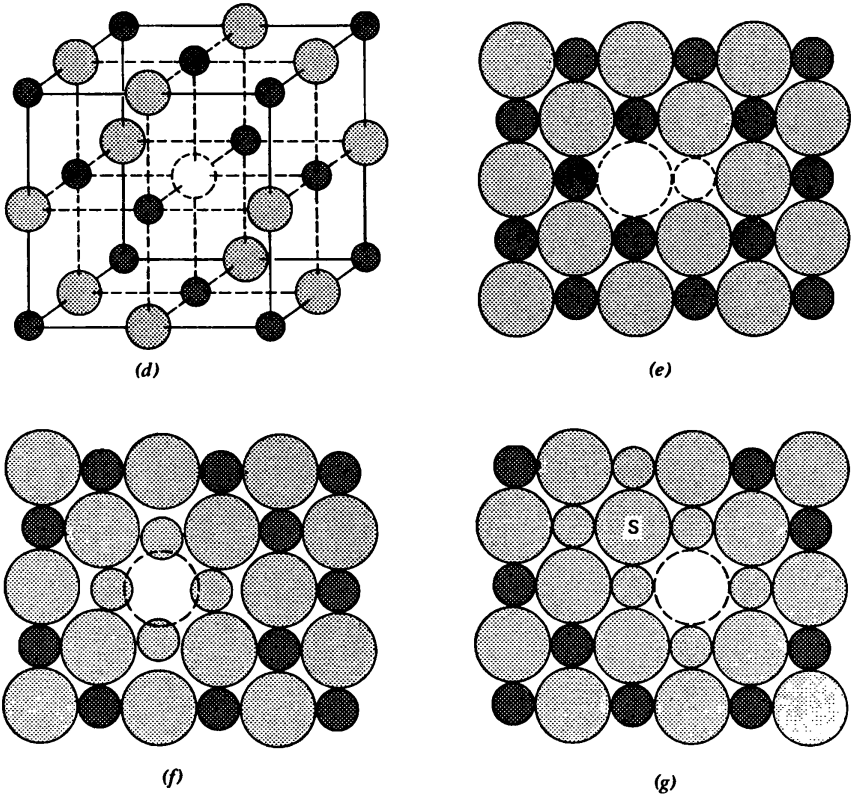

Figure 4. (*continued*)

of halogen release from the crystal. The halogen atom, produced by the photorelease of its electron, cannot be allowed to combine with free silver, as this would result in the destruction of the latent image. At first it was assumed that halogen atoms would be immobilized by the lattice structure and that attack on the latent image would not be possible except under special conditions. But halogen atoms can move through the lattice without an actual physical movement of the atom. If an electron from a neighboring halide ion moves to the halogen atom, a halide ion is formed. The donor of the electron becomes a halogen atom. Thus, the halogen atom has effectively moved one lattice spacing by the transfer of the electron. By this simple transfer of electrons, ions and atoms change places. The halogen atom acts like a positively charged electron, which solid-state physicists describe as a "positive hole." Since the movement of positive holes involves only the movement of electrons, their movement is more rapid than that of silver ions. To make a stable latent image mechanism possible, any theory of the

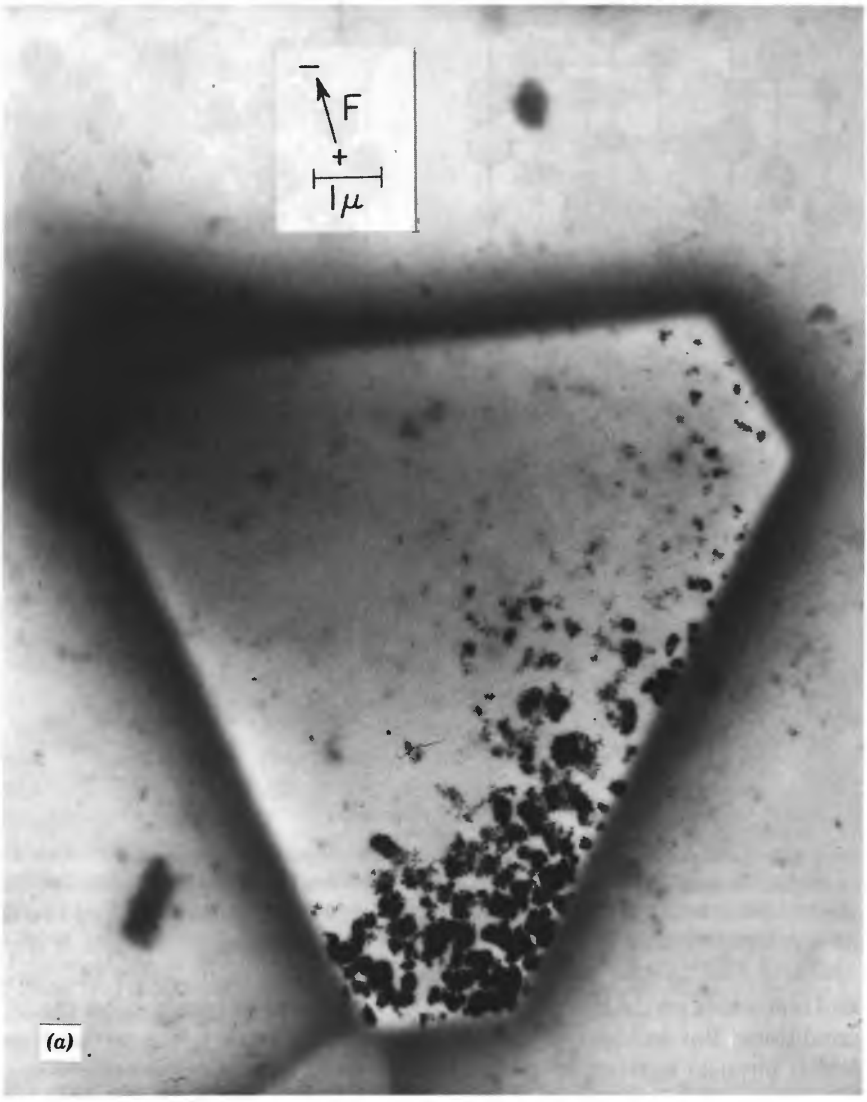

Figure 5. Electron micrographs of photographic grains showing print-out silver displaced by application of an electric field applied synchronously with repetitive light flashes. (*a*) The arrow indicates the direction of the electric field. The positive holes escape from the grain as bromine atoms and combine with the gelatin to form the dark asymmetric cloud. (*b*) Random formation of print-out silver and symmetrical escape of bromine atoms occurs when no electric field is present. (John F. Hamilton, Eastman Kodak Company)

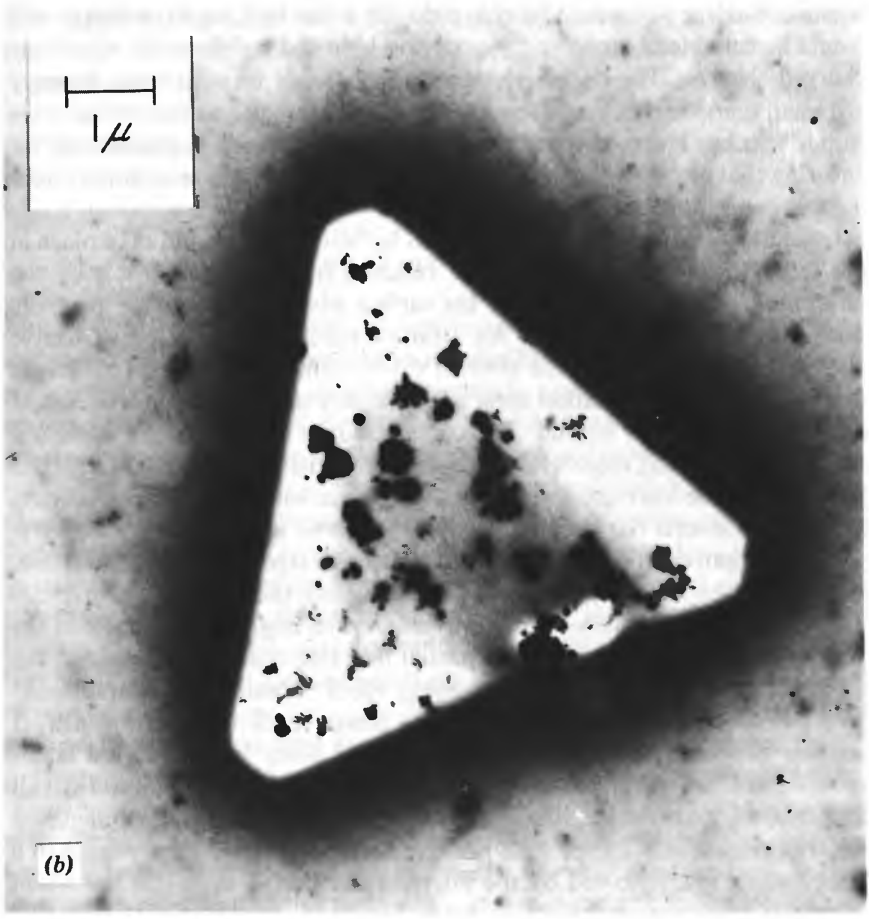

Figure 5. (*continued*)

latent image must propose a mechanism that would provide for a trapping of halogen atoms. (See Figure 5.)

In an effort to provide a more complete explanation J. W. Mitchell proposed a new mechanism of latent image formation.[41–44] The Mitchell theory provides a different trapping site for the electron and the halogen atom formed by the absorption of a light quantum. The site for the trapping of the photoreleased electron is a surface imperfection of the crystal, where the layer of alternating ions does not form a perfect layer. Here, a silver ion at the edge of the imperfection would have an effective one-half positive charge, because it is not completely surrounded by atoms that would neutralize this charge. Such a positively charged silver ion would attract the negatively charged electron and repel the positive hole. A bromide ion at

a similar surface site would be charged with a one-half negative charge and would be capable of attracting the positive hole and repelling the negatively charged electron. The positive hole would probably be even more strongly attracted to a doubly charged negative sulfide ion on the surface of the silver sulfide specks. Thus, Mitchell's proposal would provide a mechanism for ensuring that electrons and positive holes could not easily recombine under normal conditions.

Latent image formation, as envisioned by Mitchell,[45] would take place in the following manner. The electron released from the halide ion by the photon of light would migrate to the surface silver atom with the partially unneutralized positive charge. An atom of silver results with an effective one-half negative charge. This atom of silver is unstable, and the next stages of the latent image formation must occur rapidly or the electron will escape, leaving the silver ion behind. The corresponding positive hole (halide ion without its electron), meanwhile, has migrated either to the partially charged surface bromide ion or to a sulfide ion at a silver sulfide speck. The positive hole then converts the bromide ion to a bromine atom or forms a singly-charged, negative sulfide ion from the double-charged negative sulfide ion, resulting in the freeing of a nearby silver ion from the lattice structure.

The released, positively-charged silver ion then migrates to the site of the nearby single silver atom with its partial negative charge. The ion and the atom combine to form a prelatent image speck. Though still unstable, the now partially positive charged, prelatent image speck can serve to attract another photoelectron and another interstitial silver ion, yielding a latent subimage of two silver atoms and one silver ion. This combination is still unstable, as it could be attacked by positive holes. A third sequence of electron release and trapping, of positive hole trapping and the release of a lattice silver ion, followed by the migration of the silver ion to the latent subimage is necessary before a three-silver-atom latent image is formed that is stable. An interstitial silver ion is finally presumed to adsorb to the latent image site, giving it a partial positive charge. This positively charged latent image would repel the attack of the positive holes and serve as an attraction to the negatively charged developing agents during development.

The Mitchell theory was attractive because of its completeness. But the necessity for a silver ion, resulting from the trapping of the positive hole, to meet the photoelectron at a specific silver ion surface site is a complex mechanism that has brought some criticism; and this mechanism must be repeated three times before a stable latent image site is produced. In a recent review of the Mitchell theory, J. F. Hamilton and L. E. Brady[46] concluded "that the most reasonable working hypothesis for explaining photographic phenomena and designing new experiments is one based largely on the original Gurney–Mott mechanism, refined and modified by the many

contributions of a large body of photographic scientists throughout the world." W. F. Berg[47] in 1963 observed that "The Mitchell theory will keep photographic scientists busy, both experimentally and theoretically, for many years to come." The Mitchell theory certainly stimulated much activity in the field of latent image studies, but many scientists now feel that it has been disproven in some of its aspects.

CURRENT OBSERVATIONS ON LATENT IMAGE FORMATION

Although the true mechanism of latent image formation is not known now, and may never be, understanding of the mechanism has advanced through the probing experiments of photoscientists. Four species appear to be involved.[48] Light energy is absorbed by a halide ion in the lattice, freeing a negatively charged electron and leaving an uncharged bromine atom (positive hole). The positive charge results from the unneutralized charges of nearby silver ions in the silver bromide lattice. In the silver halide crystal lattice, thermal energy causes a lattice silver ion (positively charged) to move to an interstitial position, leaving behind a silver ion vacancy that is effectively negatively charged by the surrounding bromide ions of the lattice. The electron, once freed by a quantum of light, wanders throughout the crystal, both at normal and at low temperatures. The interstitial silver ion wanders through the crystal structure even in the dark, without light exposure, but its formation and movement are strongly hindered by low temperatures.

The positive hole and the silver ion vacancy may move by a replacement mechanism. An electron from a nearby bromide ion may jump to the positive hole, forming a bromide ion, but the bromide ion supplying the electron has now become the positive hole. Thus, the hole has advanced one lattice position. A repetition of this mechanism moves a positive hole through the lattice without the need of physically moving the bromine atom. A nearby silver ion in the lattice can jump into a silver-ion vacancy, thus shifting the vacancy through the lattice structure. A hole and a silver-ion vacancy can combine to form a neutral or "V" center. All four species—electron, positive hole, interstitial silver ion, and silver-ion vacancy—are mobile, and recombination must be prevented or the effect of the light exposure may be lost.

J. P. Galvin[48] has pictured the first stage of latent image formation as shown in Figure 6.

Galvin has written that

> The V center must be unstable in the surface regions, probably because the vacancy concentration is lower. The surface acts as a sink for the V centers and draws them from the interior. Thus the picture of hole mobility is of the holes spending most of the time trapped as V centers. The V centers (or the free holes after the decomposition of the

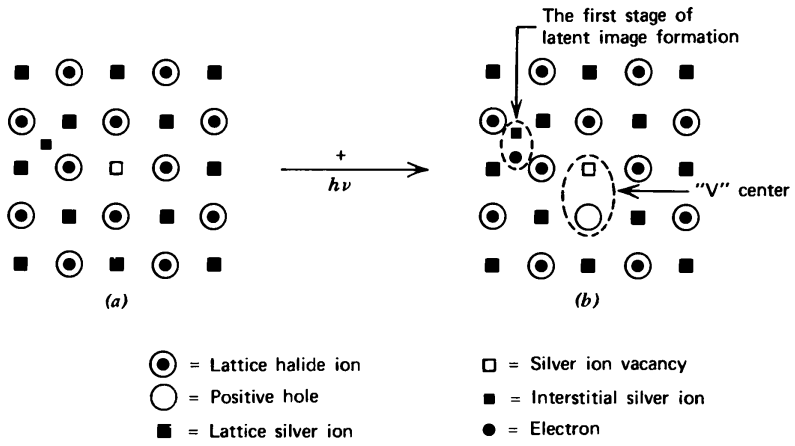

Figure 6. Representation of first of latent image formation. (*a*) A silver halide crystal, showing an interstitial silver ion and a silver ion vacancy. (*b*) The crystal after exposure with light energy (*hν*). The photoelectrons and interstitial silver ions combine to form a latent image; the positive holes and silver ion vacancies can combine to give a neutral or "V" center.

V center) move in a random fashion through the crystal. However, the V centers are unstable near the crystal surface, and so the net result is the movement of holes out of the crystal, followed by various reactions with sensitizers, gelatin, etc., at the surface.

Just as the silver latent image is formed at a few sites in the grain so that several silver atoms are formed close to each other, it seems reasonable that there will be preferred points for collection of the V centers at the surface. If two V centers arrive at a [100] crystal surface adjacent to each other, after the holes have left, either as atomic or molecular halogen, there will be a square pit one layer deep on the crystal surface caused by the absence of four lattice ions." Galvin concluded, "Thus an exposed silver crystal has two distinct latent images. These are the well-known metallic silver specks and the so-called "complementary" latent image. Both play important roles during the development process.

The need to understand the interaction of the four species that appear to be involved in latent image formation has produced a considerable volume of research effort.[49–52] V. I. Saunders, R. W. Tyler, and W. West[53] have reported that

In crystals excited in the absorption band of the silver halide, the mean lifetime of photoelectrons is ~ 0.1 μsec; that of holes is ~ 2 μsec in the interior, less at the surface. Photoelectrons and photoholes are trapped independently; their lifetimes are not determined by recombination at any value of field strength or intensity examined. The trapped charges persist with a mean lifetime of ~ 100 μsec, being neutralized by diffusion of ionic carriers of the opposite sign present in the crystal. The Gurney–Mott

scheme of latent image formation is verified with respect to the two-stage, electron-silver ion process; and, moreover, holes are trapped and neutralized by a completely analogous process.

Latent image processes are thought to involve crystal disorders and crystal impurities. The preferred sites for latent image formation were sought by G. C. Farnell, R. B. Flint, and J. B. Chanter[54] using a technique of partial development of the exposed grains and then forming photolytic silver to decorate the disorder. They found that "Many of the surface latent-image specks are formed where lines of platelets of photolytic silver meet the grain edges. It is concluded that in grains of the above type there may exist at least one specific type of disorder which provides surface sites where nucleation and aggregation of silver occur preferentially at small exposure." H. E. Spencer[55] has found in a model silver bromide emulsion that the silver sulfide sensitizer centers trap electrons but the silver sensitizer centers trap holes. (See Figure 7.)

One current mechanism of the photographic process is summarized in the following quotation from J. Malinowski:[56]

The experimental evidence now available now favors the assumption that in less than a microsecond both holes and electrons, released on the absorption of light quanta in a silver bromide grain, are independently and separately trapped. According to the transport mechanism of Gurney and Mott, interstitial silver ions neutralize the trapped electrons, forming in this way the silver atoms of the latent image specks. The temperature dependence of the lifetime and mobility of photoexcited holes indicate that, in

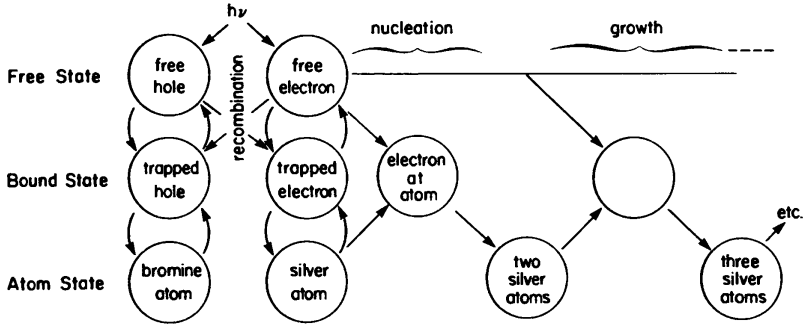

Figure 7. Model of latent image formation. Absorption of a quantum of light energy produces a free electron and a free positive hole. The possible interactions of these two carriers have been given by J. F. Hamilton in a model of latent image formation [from *Photo. Sci. and Eng.*, 18: 371 (1974)]. A three-way reversible cycle exists with free, bound, and atom states. Latent image formation requires the capture of free electrons by the atomic silver center until the size of the silver center is capable of catalyzing development.

the volume of the crystal, trapped holes are also neutralized by mobile point defects of the lattice. Silver ion vacancies are likely to participate in this neutralization process forming complexes with the trapped holes. Diffusion studies of photoexcited holes have indicated an apparent diffusion coefficient of these complexes comparable with the mobility of other ionic defects of the crystal lattice. The hole complexes were found to dissociate on the surface of the crystals, thus establishing a concentration gradient relative to the interior. In this way, the bromide equivalent to the photolytic silver formed during exposure is transferred on the surface of the grain.

The scientific knowledge gained in 100 years of gelatin–silver halide photography has not been sufficient to predict incontrovertibly the mechanism of latent image formation. New proposals continue to be made, such as the physical chemical theory of K. V. Chibisov, et al.[57] New insights are gained, however, because each new proposal of latent image formation provides the basis for new experiments to substantiate or disprove the new theory. But it is fortunate that the manufacture or treatment of photo materials is not dependent upon a complete knowledge of latent image mechanism. In fact, G. I. P. Levenson[58] has pointed out that "The history of photographic chemistry is without an example of a major innovation arrived at from theoretical, fundamental studies without some empirical discovery."

LIMITS OF THE PHOTOGRAPHIC PROCESS

The history of light-sensitive photographic materials has been marked by ever-increasing emulsion sensitivity, by broader and improved spectral response, and by finer-grained images of improved definition. It is a common event for the large photographic manufacturers regularly to introduce new products that show significant improvement in film speed and image graininess over the previous products. These advances represent a better utilization of the basic photographic process, but such improvements cannot continue indefinitely. The practical and theoretical photographic limits of the ultimate material are of great concern to photographic scientists, so much so that entire scientific conferences have been given over to a discussion of the ultimate sensitivity of photography. Just what are the possibilities and limits of the future photographic process? (See Figure 8.)

There are some practical limits. Current photographic materials are responsive to the entire range of visible light and can be made sensitive to infrared radiation. Further extension into the infrared is restricted, however, because any further extension into this region would make the photographic emulsion sensitive to heat radiation. Such a sensitized infrared material

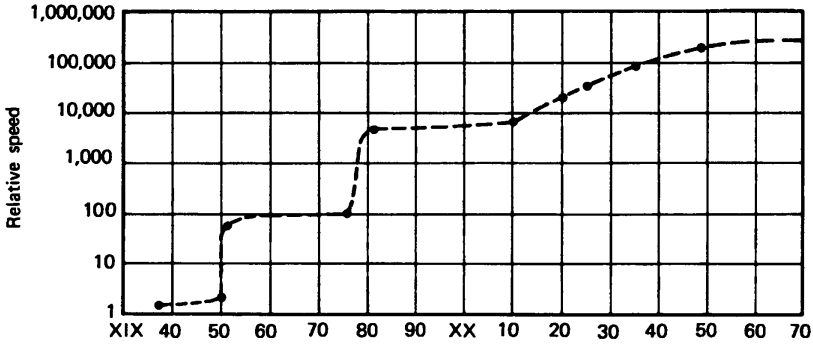

Figure 8. Growth of the speed of photographic materials. Since the invention of photography, the speed of photographic materials has increased about one million times, according to the estimate of K. V. Chibisov [*J. Phot. Sci.*, 9: 26 (1961)]. The speed of the Daguerreotype plate has been taken as unity. Relative speed is given along the vertical scale; the horizontal scale shows the years since the origin of photography (centuries in Roman numerals, decades in Arabic numerals). The first sharp jump in speed occurred with the change from Daguerreotype to wet plates; the second jump with the change from wet plates to dry silver halide–gelatin materials.

would fog spontaneously during storage. Extension of the sensitivity of the emulsion into the ultraviolet region is limited by the absorption of this radiation by glass camera lenses and the photographic material itself, although silver halide is responsive to ultraviolet. A. P. H. Trivelli[59] concluded that the maximum sensitivity of photographic materials would occur in the far ultraviolet, requiring only one quantum to make a grain developable. Image gradation would suffer because of the greater scattering of the radiation of shorter wavelength in the emulsion layer.

Much of the conjecture concerning the future of the photographic process is concerned with the ultimate sensitivity and graininess, as these two properties are interrelated. Sensitivity is determined by the quantum threshold of the individual grains—that is, the number of photons that must be absorbed to make the individual grains developable. The number of absorbed photons needed for developability, according to H. Frieser,[60] "is nearly independent of the grain size if the grains have been ripened to maximum speed." Approximately 10 to 25 absorbed photons, on the average, are required to make most of the grains developable. Many investigators have speculated that the most sensitive grains would require at least four absorbed photons to confer developability.[61] Frieser notes that since the sensitivity increases with the third power of the mean diameter of the grains, it should be possible to reach any sensitivity by increasing grain size. In modern high-speed emulsions the large grains require more photons than normal emulsion grains to become developable, thus imposing a limit on increasing

speed simply by increasing grain size. Large-sized emulsion grains generally appear more sensitive than smaller grains simply because, owing to their larger volume, they absorb more photons. The reason for the lowered sensitivity of the larger grains may be that the grain is subdivided into regions which act independently during exposure.[62] Increasing grain size would also adversely affect the reproduction of fine image details because of the effect of the distribution of the larger grains and the increased light scatter in the emulsion layer.

H. Frieser[60] concluded, "It is obvious that a layer with grains of uniform size and a quantum threshold of four photons per grain, which is the theoretical limit according to Mitchell, is approximately ten times more sensitive than a commercial layer of the same grain size. An emulsion with grains of quantum threshold four whose grain size is not constant could have a still higher sensitivity."

E. Klein[63] estimated that if grains could be made developable by only one quantum of light, the increase in sensitivity would be only four times. If all the grains were of the same sensitivity, an image of very high gradation would be obtained. Klein also noted that "With practical emulsions, the total absorption is of the order of 50 percent. Theoretically, a maximum increase of 50 percent can be obtained if absorption in the emulsions can be increased (raising the absorption coefficient of AgHal, modification of the paths of light by alteration of the scattering conditions in the emulsion layer)." Klein concluded that the exploitable sensitivity of a one-quantum-per-grain emulsion might be increased by about 10 times.

The perfect photographic detector would require only a single incident photon to make the grain developable. Statistical fluctuations in the incident photons and fluctuations in the number of grains made developable by a given exposure make it impossible to achieve a quantum efficiency of one. In a theoretical study of the quantum efficiency of photographic detectors Hans J. Zweig[64] concluded that

> the signal which can be detected may be smaller for grains requiring many photons for developability than for those requiring only a few photons. This is true when the signal to be detected represents a small increment on a strong background radiation. It is also shown that, in order to optimize the quantum efficiency for a wide range of background radiation strengths, a mixture of grains requiring different numbers of photons for developability is needed. Quantum efficiency should therefore be related to latitude. For a latitude such as required in pictorial work, the optimum *uniform* quantum efficiency that can be achieved with a photographic type of detector compared with a perfect detector is between 2.5 percent and 5 percent. This means that actual emulsions which have, at present, a quantum efficiency of between 0.5 percent and 1 percent differ from the attainable optimum by a factor of between five and ten.

In 1946 Albert Rose[65] showed that the efficiency of radiation-sensitive elements as different as television tubes, the human eye, or photographic film could be compared by considering their signal-to-noise ratio. For photographic film the signal is related to the optical density produced after development and the noise is related to the granularity of the developed image. The term "detective quantum efficiency" was originated by R. C. Jones[66] to describe the signal-to-noise ratio of a real detector to the same ratio of a ideal detector:

$$\frac{(\text{signal/noise})^2_{\text{real}}}{(\text{signal/noise})^2_{\text{ideal}}} = \text{DQE}$$

where DQE represents the detective quantum efficiency.

Much discussion has centered around the various factors that influence the DQE.[67–73] G. R. Bird, R. C. Jones, and A. E. Ames,[74] for example, concluded that the recombination of photoelectron-hole pairs would be the major cause of inefficiency in giving low quantum yields. About 30 photons per grain would be necessary to make 50% of the grains developable. H. E. Spencer,[75] however, felt that the maximum quantum efficiency would occur when only three to four photons per grain caused less than 10% of the grains to be developable. A. Marriage[76] has stated that photon noise would have no effect on granularity, granularity being the result of the grain structure of the photographic layer. The use of detective quantum efficiency as a performance rating may not be the most useful for some photographic materials, such as those for astronomical uses.[77] H. F. Nitka[78] proposed that the best exposure for low light levels of a photographic material may not be the exposure necessary for the maximum detective quantum efficiency.

Unconventional photographic processes have been suggested as a means to achieve higher sensitivities that approach the higher sensitivity of the photoelectric type. According to J. D. McGee,[79] "The efficiency of conversion of photons to electrons by an efficient modern photocathode (i.e., the photoelectric quantum efficiency) is about ten percent or about two orders of magnitude greater than the corresponding figure for the efficiency of activation of silver halide grains by photons incident on photographic emulsion, which is about 0.1 percent." R. Shaw[80] suggested unconventional silver halide grains that at 100% DQE would be limited only by the quantum nature of the exposure itself: "Calculations show that this could probably mean acceptable photographs by starlight." (See Figure 9.)

The limits and possibilities of the photographic process continue to be of importance to both the theoretical worker and the manufacturers of photomaterials. The ultimate sensitivity of future photographic emulsions cannot

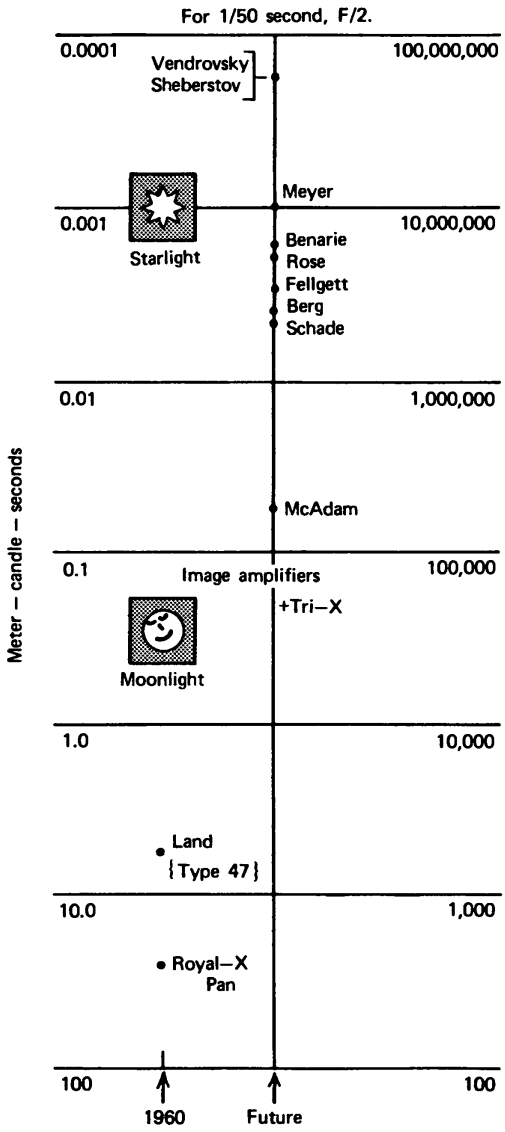

Figure 9. In 1960 eminent photographic scientists were asked to estimate the ultimate speed in photography, which was stated to be the least level of illumination that would allow a picture to be taken at $\frac{1}{50}$ second at f/2. The pictorial record was to be in the form of a large snapshot, 9 × 12 cm, of just acceptable quality. The review of estimates of ultimate speed, as given by E. W. H. Selwyn [*J. Phot. Sci.*, 9: 258 (1961)] in the diagram, indicated that ultimately it may be just possible to take snapshots by starlight.

be estimated precisely, because the history of photographic manufacture has been concerned with many technical advances that are the result of advances in photographic chemistry. Chemical and spectral sensitization, as well as other chemical addenda, have greatly contributed to improved speed/grain characteristics of photographic emulsions. Improved chemical compositions in the developing solutions have also aided the technological improvement of the photographic process. Current estimates of the future of photography cannot anticipate what the chemical advances of the future will be; rather, they are based on the present chemical compositions of the emulsion and processing solutions. There are certain inherent limitations to detectors of the silver halide type, but a photographic emulsion capable of use in moonlight would satisfy most photographic requirements. This writer feels that the advance of photographic chemistry in emulsion compositions, particularly with incorporated processing chemicals, plus new methods of image processing, will provide photographic materials that should match or exceed the current efficiency of photoelectronic detectors and have superior image definition.

STABILITY OF THE LATENT IMAGE

The latent image resulting from an instant of light exposure is usually developed days or weeks after the exposure. Accounts are not uncommon of exposed film existing many tens of years before development. As might be suspected, an invisible image of four, 10, or even 100 silver atoms may be subject to change with time. Changes in the first few microseconds after exposure would be of interest to phototheorists and changes after that to all who would use photography for precise image recording. But the nature of any change is in doubt. Both a growth and a fading of the latent image have been reported. A good review of the extensive literature on this subject has been given by Hans Eduard Keller.[81]

Early in the dry-plate period of photography many photographers believed that holding an underexposed silver bromide plate for a few weeks or months before development would compensate for the insufficient exposure. In 1889 Thomas Bedding[82] denied this continuing action of the effect of light by calling this belief a "photographic heresy." But Charles Brush[83,84] in 1910 stated that "Photographic action, when fully excited, *continues many minutes after exposure*, gradually dying out. With the adopted period of exposure, this after action amounts to something like eight or ten percent of the whole. Within an hour or two after the action has ceased, relapse sets in and amounts to about four percent the first thirty hours,

fully half of which occurs within the first four hours." Clarence E. Weinland failed to duplicate the claim of Brush.[85]

Although not confirming Brush's results, other investigators, including C. E. K. Mees[86] in 1915, reported increases in film speed upon aging the latent image. M. C. Jausseran[87] in 1929 and E. R. Bullock[88] and Philip C. Keenan[89] in the early 1930s found a spontaneous reinforcement of the latent image upon standing after formation. Many of these early investigators searched for changes in the latent image during only the first few seconds or minutes after exposure of the photographic emulsion. Many of these efforts were seeking information for interpreting the current theory of latent image formation.

The latent image formed by low intensities of light was found to regress to a greater degree than the image formed at high intensities during the experiments of J. Eggers, R. Matejec, and R. Meyer.[90] Latent image regression was found by Erwin Heisenberg[91] to be changed into intensification if the alkalinity of the coated emulsion was raised. Certain sensitizing dyes (imidacarbocyanines) have been found to repress latent image fading or actually intensify it.[92] Gelatin is believed to have a stabilizing effect on the latent image.[93,94]

In 1941 K. Famulener and E. Loessel[95] studied the practical effect of a delay between exposure and development of modern motion picture films in terms of film speed, gradation, and graininess. Their study extended over a period of one year. The latent image of panchromatic negative films increased from $\frac{1}{2}$ to $2\frac{1}{2}$ stops in speed during a one-year storage of the latent image under average conditions. A decrease in gradation and a slight increase in graininess was also found to have occurred. Unsensitized films either showed no speed gain or some fading of the latent image upon storage. But it was not possible to establish any definite law of latent image growth with time for the panchromatic film materials. Keith Famulener and Stanley L. Judkins[96] confirmed these results. They found that high humidities produce a growth in the low to medium densities, a loss in the high densities.

The latent image fading of three commercially available, fine-grained films has been studied by R. A. Armistead and F. B. Galimba.[97] Kodak Fine-Grain Positive Film had a moderate fading rate of the latent image in the higher densities but latent image growth for densities less than one. Kodak SO-343 film had a rapid fading rate for all densities, but Kodak Commercial Film had only minor fading. It was concluded that oxygen played a dominant role during changes in the stability of the latent image. Henriette Faraggi and Georgette Albouy[98,99] also found that oxygen from the air was the primary cause of the destruction of the latent image.

Many reports have continued to be published concerning the practical effect of storage of exposed photographic materials. In a recent summary

Gary A. Micanek[100] listed the following 14 factors that had been previously reported to affect latent image stability:

1. Time of storage.
2. Temperature of storage.
3. Relative humidity in storage.
4. Spectral sensitization of the emulsion.
5. Relative emulsion sensitivity.
6. Chemical sensitization of the emulsion.
7. Wavelength of the exposing illumination.
8. Nature of the film or paper support.
9. Emulsion alkalinity and silver-ion concentration.
10. Manufacturing techniques.
11. Atmosphere during storage interval.
12. Silver halide type.
13. Development time.
14. Development strength.

The first four factors (time, temperature, and humidity of storage and the type of spectral sensitization of the emulsion) are thought to be the most important in affecting latent image stability. These factors were then studied using the same halide emulsion with different degrees of spectral sensitization. The following conclusions were stated:

1. The latent image is not stable with time and shows a decided growth with age; it is not expected that storage well below zero would preserve the latent image indefinitely.
2. The latent image is highly influenced by temperature. Rapid deterioration of images occurs at 120°F.
3. Storage at slightly above freezing is not nearly as desirable as storage well below zero.
4. The humidity at which the film is stored accelerates the growth in all densities throughout the characteristic curve. In general, this effect is much less than the effect of temperature.
5. The growth effect may depend on the optical sensitization of the emulsion. The unsensitized emulsion showed the least growth in the latent image.

Fading of the latent image has also been reported. Agfa Diapositive plates showed latent image fading according to M. C. Hylan and J. M. Blair.[101] They felt that heat during storage had an effect similar to faint illumination of long-wavelength light—that is, a dispersing effect on the silver atoms of the latent image. K. B. Mather[102] studied the latent images given by proton

tracks, finding that the fading is only 10% with storage in vacuum as compared to the fading in air. Image fading has been of concern for monitoring X- and gamma radiation.[103,104] Latent image fading in nuclear emulsions with their low gelatin content has been widely observed. A summary of the investigations of G. Albouy and H. Faraggi[105] on this subject is given below.

1. At constant humidity the rate of fading is an exponential function of the absolute temperature.
2. At constant temperature the rate of fading is an exponential function of the quantity of water retained by the gelatin.
3. At constant temperature and constant humidity fading is twice as rapid in pure oxygen as in air and 10 times more rapid in pure oxygen than in nitrogen. When the plates are stored in dried inert gases, fading practically vanishes.
4. Fading occurs more rapidly the finer the grain size of the emulsion.
5. All substances having an alkalinity greater than that of the emulsion stabilize the latent image, and all substances having acidity lower than that of the emulsion produce accelerated fading.

The mechanism of the fading of the latent image is still unresolved. A thermal mechanism has been proposed in which heat energy supplies the necessary energy to liberate an electron from the latent image, resulting in a dispersal of the latent image by a process that is the reverse of its formation.

$$\underset{\substack{\text{metallic}\\\text{silver}\\\text{(latent}\\\text{image)}}}{Ag} \longrightarrow \underset{\substack{\text{silver}\\\text{ion}}}{Ag^+} + \underset{\text{an electron}}{e^-}$$

Another proposal depends upon a chemical attack on the latent image, possibly by the oxygen of the air, to convert the silver atoms into an oxide or other form that would not be suitable to catalyze development.

$$\underset{\substack{\text{metallic silver}\\\text{(latent image)}}}{2Ag} + \underset{\text{oxygen}}{O} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\substack{\text{silver}\\\text{ions}}}{2Ag^+} + \underset{\substack{\text{hydroxyl}\\\text{ions}}}{2OH^-}$$

Eggers et al.[90] have suggested that the internal latent image exhibits early fading, building up the surface latent image. A. L. Kartuzhanskii and A. F. Yurchenko[106–108] feel that the internal image is intensified by electrons' being transferred from the surface latent image that is being dissociated into silver ions and electrons.

S. M. Solov'ev[109] found that "Oxygen has no effect on the latent image obtained on a fast panchromatic film," while S. G. Grenishin,[110] using three types of exposing radiation, reported that "Fading basically is caused by the oxidation of latent image centers by the air oxygen in the presence of

moisture included in gelatin." As long as experimental conditions differ, it appears that experimental conclusions will continue to differ concerning the stability of the latent image.

In his excellent review of the effects of environment on latent image formation by light T. H. James[111] examined the conflicting mass of published results, concluding, "No conclusion can be reached at this time." James also added that the possibility might exist that the thermal and oxidation theories of latent image fading may be both parts of the same mechanism that destroys the latent image silver. He also observed that the different results obtained by different investigators may be related to their use of different photographic emulsions, as no contradictory results have been reported for the same emulsion.

STABILITY OF PHOTOGRAPHIC PRODUCTS

The characteristics of the developed photographic image, either dye or silver, are influenced not only by the latent image keeping but by the entire history of the photographic material during manufacture and its storage before exposure. High temperatures and humidities are known to cause a loss in sensitivity, lower gradation, and increase the background density on black-and-white photographic materials.[112,113] With color materials the loss in sensitivity may not be the same for each of the three color-sensitized layers, thus causing the color balance of the image to shift. The gradation of each layer may also increase or decrease, producing false coloration in high- or low-exposure areas when the medium-exposure areas are neutral.[114] Obviously, protecting the emulsion before exposure and continuing the safeguards after exposure are essential not only for valid comparisons during latent image keeping studies but also for every processor of photographic materials if consistent results are to be obtained. Prompt processing of film after exposure will minimize latent image changes.

Before processing, photographic materials are subject to deterioration by extremes of temperature and humidity, harmful gases, X-rays and other radiation, and physical pressure.[115,116] Oxygen, according to T. D. Smith,[117] accelerates the loss of film speed but helps to decrease the overall fog that forms with long-time storage of silver halide emulsions. This age fog is probably the result of complex chemical interactions but may represent a continuation of the chemical ripening that occurs during the steps of emulsion making. Most film products are sealed to exclude continued effects due to the presence of atmospheric oxygen, but exposed film is usually not as well protected. Other gases, such as ammonia, formaldehyde, fumes from furnaces

and cars, hydrogen sulfide, mercury, and sulfur dioxide, are deterimental to photographic materials. Peroxides, such as those coming from drying paint or varnishes, also have an adverse effect on the stability of films or papers. Storage of unprocessed film in a freshly painted drawer has been found to give rise to erratic photographic results.

Photographic emulsion layers are sensitive to light energy but also to other kinds of radiation. Although one-tenth of the energy coming into the earth's atmosphere is in the form of cosmic rays,[118] such energy was not found by Wayne T. Sproull[119] to be responsible for the deterioration of photographic films before development. Modern high-speed, X-ray films do increase in background density as a result of prolonged storage under room conditions. This increase in density, according to Donald P. Jones and Robert H. Barber,[120] is related to the sensitivity of X-ray film to the high-energy background radiation of cobalt-60. It was noted that the normal background density growth during storage of a variety of photographic films was related to their relative sensitivity to cobalt-60 gamma radiation.

Moisture, accentuated by the thermal effects of temperature, has a deleterious effect on photographic materials either before or after exposure. High-relative-humidity conditions during storage of photographic emulsions have been reported[121] to cause irreversible changes in sensitivity centers and may even change the sensitizing dye. Both the surface and internal sensitivity centers are adversely affected by moisture during storage.

Temperature and moisture appear to be the most detrimental factors for both exposed and unexposed silver halide materials. Film products in sealed containers usually are unaffected by moisture, but the temperature of storage depends on many persons in the manufacturer-to-consumer chain. Vaporproof packages are not heatproof.[122] The listing of expiration dates on photographic materials is an estimate of time that a photographic product will stand average storage conditions and still give a satisfactory result, but a film nearing its expiration date will not yield results identical with those of fresh film. Thus, the history of the film after manufacture is an important factor in determining the results possible from photographic processing. (See Figure 10.)

Film in a vaportight package or container may be temporarily stored in a refrigerator operating at 40 to 50°F. For extensive periods of storage a deep-freeze unit operating at 0 to -10°F is to be preferred.[123] At these temperatures or even lower the aging of film is interrupted, as heat is a major cause of film deterioration; aging will begin at its normal rate when the film is returned to normal temperatures. Film removed from a refrigeration unit should not be used until it reaches equilibrium with the surrounding atmosphere. Moisture may form in droplets on the film base and emulsion surface if the cold film is opened in air of high humidity. The warm-up time

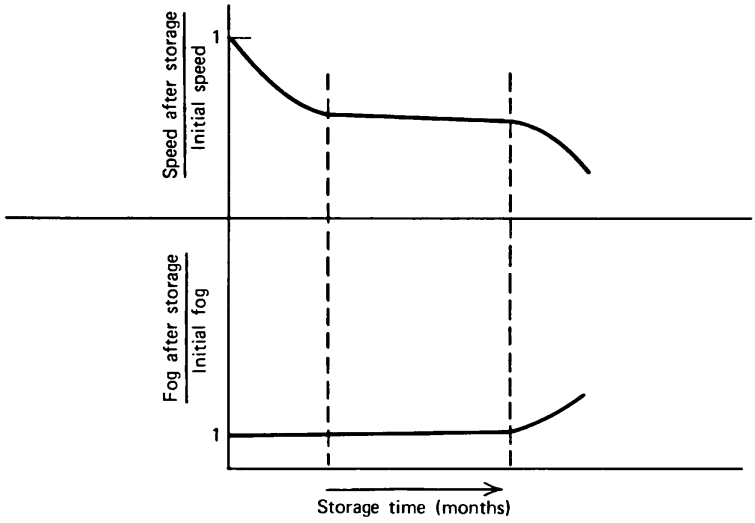

Figure 10. Schematic diagram of the change in speed and fog density of four amateur negative black-and-white films during storage and natural aging, as found by Z. I. Shavrova [*Zhur. Nauch. Prikl. Fot. Kinemat.*, 17(5): 389 (1972)]. A stable plateau was reached after the initial speed loss. The plateau was followed by a rapid loss in sensitivity with a simultaneous growth in fog.

of refrigerated film depends upon the packaging and the temperature differential. For commercially packaged film the following warm-up times have been proposed[124] to avoid moisture condensation.

	Time (Hours) to Avoid Moisture Condensation for a Temperature Rise of	
Film Type	25°F	100°F
Roll film (including 828)	½	1
135 magazines and 126 cartridges	1	1½
10-sheet box	1	1½
50-sheet box	2	3
8 mm, any length	1	1½
Super-8 cartridges	1	1½
16 mm, any length	1	1½
35 mm, any length	3	5

Film that has been removed from its vaportight package or container, such as exposed film, should not be put directly in the refrigerator but placed first in a jar or other container which can be closed with an airtight seal. At 50% relative humidity, photographic film emulsions contain about 8% moisture. However, film is often used under very humid conditions. In this case some moisture should be removed from the emulsion. Silica gel was found to be the most satisfactory of all the desiccants tested for this purpose by C. J. Kunz and C. E. Ives.[125] However, these investigators warn that dehydrated film should not be unwound until the film has regained some moisture by conditioning at normal conditions.

For drying color films from equilibrium at 80% to equilibrium at 40% relative humidity, activated silica gel in the following amounts will require the times listed below.

Quantity of Kodak Color Film	Quantity of Silica Gel	Approximate Drying time
10 sheets, 5 × 7 in. (plus interleaving paper and cardboard stiffeners)	1 oz	1 wk
20 rolls 620 or 120	5 oz	2 wk
20 magazines 135, rolls 828, or cartridges 126	1 oz	2 wk
10 rolls, 8 mm × 25 ft	1 oz	2 wk
10 super-8 cartridges	1 oz	2 wk
10 rolls, 16 mm × 100 ft	5 oz	2 wk

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Chapter 4
Amplifying the Latent Image

The only way of deciding the answer to a practical problem in photographic chemistry is to "try it and see." Photographic emulsions are such complex things that it is impossible to predict with certainty what will happen under given conditions merely by working on theory.

G. I. P. LEVENSON[323]

The latent image may consist of from three or four to a few hundred atoms of silver. This image is too microscopic—indeed is submicroscopic—to be of any direct use. When the exposing light is able to act for a suitably long period, the photons of light eject enough photoelectrons so that their combination with silver ions causes the latent image to grow until it becomes visible. This visible or printout image has found practical use in photographic papers for proofing portraits or recording oscillographic traces, but the normal exposure of photographic films and papers does not provide enough electrons for the latent image to grow to a visible size.

Any source of electrons that might be supplied, preferentially to the latent images of the exposed silver halide grains but not to unexposed grains, would amplify the latent image to a visible size. In photographic processing the donors of electrons are called developing agents. These chemical compounds supply the electrons that may amplify the latent image as much as one billion times. Developing agents require less energy to give up electrons

to those silver halide grains that have a latent image. Thus, the exposed grains receive the electrons first and the latent image is amplified first, but some developing agents may possess sufficient energy to donate their electrons to unexposed grains. Once the growth of the center of the silver atoms is started on an unexposed grain, less energetic molecules of the developing compound can contribute their electrons. Although slow to start developing, unexposed silver halide grains may rapidly produce deposits of silver atoms that obscure the developed image of the exposed grains. This nonimage silver, called fog, is a limiting factor in the degree of image amplification that is possible.

The exposing light forms a few electrons that result in the formation of a few silver atoms on the exposed grains. At a later time the developing agent continues this process, providing the electrons that continue the image formation interrupted so abruptly when the exposure was ended. At the latent image site the electron from the developing agent molecule combines with a silver ion from the grain to form an atom of metallic silver. This is essentially the final sequence of events that occurred during the original light exposure. After a million or so silver atoms are formed, the latent image becomes visible and of practical use. When all the silver ions come directly from the exposed silver halide grain, the visible image is said to have been formed by chemical development.

There is another way that the latent image may be amplified. All of the unused silver ions, in both the exposed and unexposed grains, left after exposure may be removed from the emulsion layer. In the gelatin layer only the silver atoms of the latent image remain. For amplifying this image to practical size the developing agent is used in a solution that also contains a soluble silver salt, such as silver nitrate. The developing agent donates electrons to the silver ions in solution so that metallic silver is catalytically produced on the surface of the silver atoms of the latent image. This coating or plating of the latent image continues until the image grows to a visible size. The amplification of a latent image using only the silver ions from the developing solution is called physical development.

Most modern developing solutions do not contain silver ions but do contain substances that solubilize silver ions from the silver halide grains of the photographic emulsion. During the initial period, when chemical development may be occurring, the quantity of silver ions in the developer solution will be increasing. Eventually some of these silver ions that came from the halide grains, either exposed or unexposed, will be deposited as metallic silver upon the image silver formed by chemical development. In practice, most modern developing solutions work by this combination of chemical and physical development, often called solution-physical development.[1–4]

The developing agent is the electron donor in either the chemical or physical developing actions. In chemistry, electron donors are known as reducing agents. When the reducing agent gives up an electron, the reducing agent is changed to an oxidized form. The electron is gained by a compound that is then changed to the reduced form.[5] The oxidation number of the reducing agent becomes more positive; the oxidation number of the compound accepting the electrons becomes more negative.

In a suitable developing solution, bivalent iron (ferrous) ions act as a developing agent. This is illustrated by the equation:

$$Fe^{2+} + Ag^{+} \longrightarrow Ag^{0}(\text{metal}) + Fe^{3+}$$

A developing agent (Fe^{2+}) donates an electron to an oxidizing agent (Ag^{+}) to yield the oxidized form of the developing agent (Fe^{3+}) and the reduced form of the oxidizing agent (uncharged metallic silver).

Other compounds are present in a developing solution besides the developing agent, but these other compounds are present only to activate, restrain, or protect the developing agent. In fact, the rest of the processing cycle after development exists only to insure the permanence of the image formed by the reducing action of the developing agent. Thus, the most critical step in photographic processing is the latent image amplification by the developing agent. For this reason the major amount of chemical research is directed toward finding and using reducing agents as developing agents, and then trying to fathom the mechanisms of photographic development.

CLASSIFICATION OF DEVELOPING AGENTS BY REDUCTION POTENTIAL

There are truly tens of thousands of compounds that might serve as sources of electrons for the development process. Substances as diverse as human urine,[6] old red wine, anaerobic cultures of bacteria, polluted river water,[7] or citrus fruit juice have been reported as suitable for developing a latent image. Every substance might be considered to have a certain pressure of electrons that causes them to seek to escape. When a substance with a high electron pressure is present with a substance that has a lower electron pressure, the electrons will flow from the compound with the higher pressure to the compound with the lower pressure. To be a developing agent, a compound must have an electron pressure greater than that of solid silver; that is, the developing agent must be able to transfer an electron to silver halide to reduce it to metallic silver.

If the electron pressure of a compound is only slightly more than that of solid silver, there is a danger that the latent image may transfer an electron

to the compound, rather than the desired transfer from the compound to the latent image. A compound with a higher electron pressure would avoid this loss of latent image. However, the electron pressure must not reach such a level that an electron can be supplied to the conduction band of the silver halide crystals—that is, can flow unimpeded throughout the crystals. Such energetic electrons would cause the reduction to silver of both exposed and unexposed silver halide grains. Electrons supplied at a pressure sufficient to enter the conduction band of the silver halide grains would act exactly like the electrons formed by the light exposure that produced the latent image. If this happened, each grain would have an artificially produced latent image; and each grain, upon development, would be quickly reduced to metallic silver.

The desirable developing agent is a compound with an electron pressure sufficient to transfer an electron to a silver halide grain with a latent image but insufficient to supply an electron to the conduction band of any of the grains. The catalytic effect of the latent image allows the electron transfer from the developing agent at a pressure slightly lower than that required for the transfer to the conduction band. Because of this catalytic effect of the latent image the exposed silver halide will be converted to metallic silver before the unexposed grains are reduced.

The ease with which a substance gives up electrons (acts as a developing agent) may be measured directly. This tendency of a compound is called its potential. For a developing agent which causes silver to be reduced from the ionic to the metallic form this tendency is called its reduction potential. Potentials in units of volts are compared to each other, with one agent arbitrarily assigned a zero potential. This zero potential has been assigned to the hydrogen electrode (at unit activity of the hydrogen ion and one atmosphere hydrogen pressure). Because of difficulties in maintaining the hydrogen electrode, a normal calomel electrode is often used in its place. This reference electrode operates at a constant potential of $+0.244$ V with respect to the hydrogen electrode.

When a platinum electrode is inserted in a solution containing both the oxidized and reduced forms of a reversible developing agent, the electrode will acquire a definite potential. The potential of the platinum electrode may be compared with that of the standard calomel electrode by connecting the two electrodes into an electrical circuit. (The standard calomel electrode consists of a platinum electrode immersed in a solution saturated with respect to mercury, mercurous chloride, and potassium chloride.) The electron pressure or reduction potential of a developing agent may then be measured and expressed in volts. To reduce silver ions to silver, the potential of the developing agent must be more negative than the potential of silver. The greater the negative value of the potential, the more powerful is the

reducing action of the compound—that is, the greater the ease with which the compound gives up electrons. This measured electrode potential is referred to as the reduction-oxidation potential, or redox potential, of the developing agent.

In 1934 W. Reinders[8] showed that for a substance to be effective as a developing agent, not only must it have a potential less than that of silver (that is, less positive or more negative in value), but the potential must be a certain minimum value before development is initiated. Using various solutions of known redox potentials, Reinders reported that "The latent image of a normally exposed photographic plate is not developed unless the developer has a reduction potential of at least 70 millivolts below the silver potential in solution." This critical value of the potential was the one required to start reduction of silver ions in areas of considerable exposure. Areas of lesser exposure would require a developing agent with a more negative potential. Once the development of the latent image had started, however, a less powerful reducing agent could continue the reduction of the silver ions of the exposed grains.

Various other investigators have found the minimum values of the critical potential to range from about 50 to 160 mV below the silver potential.[9–11] If 80 mV is taken as the critical potential needed to begin development, then development should begin 80 mV below the silver potential—that is, below +0.120 V. M. Abribat[12] formulated the following empirical rule based on this concept: "Every oxidation-reduction system with a real redox potential, i.e., reversible system, or an apparent redox potential, i.e., irreversible system, which is more negative than a determined critical value for a certain emulsion constitutes a developer, whatever the structure of the developing agent."

In practice, developing solutions have a measured potential that is considerably more negative than the minimum necessary to initiate development. This greater potential is needed to prevent solubilization and thus loss of the very small latent image centers. R. M. Evans and W. T. Hanson, Jr.,[13,14] found that Kodak Developer D-76 had a negative potential of 259 mV and Kodak Developer D-72 a negative potential of 407 mV. Practical developers thus possess reducing power considerably greater than the minimum needed to initiate development of the latent image. Because of this reducing power, practical developing solutions have the capability of reducing unexposed silver halide grains if sufficient time is allowed. The meaning of the measured potential of a practical developing solution is somewhat obscure, however. Indeed, T. Howard James and George Higgins[15] state in their book that "In general, no successful correlation has yet been made between developer activity and the redox potentials of the developers."

Experiments by H. Socher[16] and others[17] have clearly indicated that the

critical potential to initiate development is at least partially related to the presence of the gelatin. Socher showed that silver bromide in the absence of gelatin did not require a potential lower than that required to reduce silver ions to silver; but when the silver bromide was precipitated in gelatin and then coated on a plate, the reduction of the silver ions of the silver bromide required a critical potential 60 mV more negative. Apparently, the gelatin either interferes with the access of the developing agent to the surface of the silver halide or reduces the dissolution or mobility of the silver ions.

Recently Rex Pontius and his co-workers[18] have examined three cases of pure physical development and found that no critical potential exists for this type of development. They have questioned if a true critical potential even exists for chemical development, stating that the "magnitude of the apparent overpotential, on this basis, may be expected to vary with the presence of substances, in addition to gelatin, which adsorb to the silver halide surface, and which may exert an influence upon the release of silver or bromide ions."

The significance of rating developing agents by redox potential measurements is still open to considerable debate.[19–20] The measurements are known to be influenced greatly by pH and the quantity of the oxidized form of the developing agent that is present.[21,22] Some developing agents seem to require the presence of their oxidized forms to be active. Other developer compounds that interact with the oxidized form affect the redox potential of a developing solution. Potential measurements do not give any information concerning the rate of diffusion of the reducing substance through the gelatin emulsion layer or the interval before the agent begins to reduce the silver ions, once it reaches the grain surface. Silver chloride grains are easier to reduce than silver bromide, and silver iodide grains are the most difficult of all. A weak reducing agent can reduce fine emulsion grains better than the coarse-grained ones. Finally, a negative redox potential does not indicate if the compound will selectively develop the latent image or completely reduce all the silver halide, exposed or not.

CLASSIFICATION OF DEVELOPING AGENTS BY THEIR STRUCTURE

The first organic developing agent was used even before the perfection of the first practical photographic process. In 1802 Thomas Wedgwood (with observations by Humphrey Davy) reported that silver nitrate coated on leather required less exposure to light to print out a visible image than when the silver nitrate was coated on paper.[23,24] This observation prompted the Rev. J. B. Reade in 1837 to repeat the experiment, borrowing a pair of kid gloves from Mrs. Reade. When Mrs. Reade objected to supplying another

pair of her leather gloves, Rev. Reade decided to "tan paper," reasoning correctly that the chemicals in the leather from the tanning process were probably causing the increased sensitivity of the silver nitrate. He used an infusion of nut galls, containing a high concentration of gallic acid, to treat his paper.[25]

Unfortunately, Rev. Reade, an amateur photographer, did not publish the results of his experiments and his exact contribution is difficult to establish,[26–28] but he showed several of his friends the successful results of his efforts. One friend, Andrew Ross, a lens maker, may have told W. H. Fox Talbot about Reade's use of gallic acid. Reade, in 1854, claimed he personally told Fox Talbot about the use of the infusion of galls.[29] Fox Talbot used gallic acid in both the light-sensitive paper and the developing solution for it. Talbot's Calotype process, introduced on February 5, 1841, was the forerunner of the type of negative-positive photography that we have today.[30,31] Gallic acid was used as a developing agent to amplify the latent image. This was the first organic compound to be used to develop the latent image.

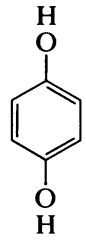
In 1851 Frederick Scott Archer[32] proposed the use of collodion, which is cotton dissolved in nitric and sulfuric acid, alcohol, and ether, as a means to adhere the light-sensitive silver salts to a glass plate. Archer developed the latent image of a still-wet plate with either gallic acid or pyrogallic acid. The latter compound was prepared at that time by heating gallic acid. (The prefix pyro, from the Greek word *pyros* meaning fire, was then customarily attached to the name of compounds prepared by heat treatment.) Unfortunately, heating gallic acid removed the —COOH group which contributed so much to the acidity of gallic acid. Although pyrogallic acid was a misnomer, this compound was a more active developing agent than gallic acid; it is now known as pyrogallol, or pyro. Pyrogallol was the second organic developing agent to be used, and it is still an important developing agent even today.

Between 1880 and 1900 most of the developing agents in use today were discovered, not only by the study of reduction potentials, but by the testing of possible agents under practical developing conditions. Most of the useful developing substances were derivatives of benzene. In 1891 Auguste and Louis Lumière[33] and, independently, Momme Andresen[34–37] began to relate developing properties to the chemical structure of all of the known organic developing agents. A. Bogisch[38,39] and B. Homolka[40–43] were also active in studying the structures of developing agents. By 1922 A. H. Nietz[44] was able to summarize the Lumière–Andresen rules for the structure of a developing agent. Any compound that satisfied the structural requirements should be a developing agent; all those compounds that did not comply should have no developing action.

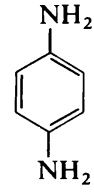
Lumière-Andresen Rules

According to the Lumière-Andresen rules for the structure of organic developing agents, benzene derivatives were developing agents if:

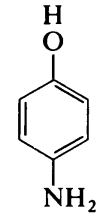
1. At least two —OH, two —NH_2, or one —OH and one —NH_2 groups were attached to the benzene ring, as in:



hydroquinone

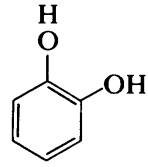


p-phenylenediamine

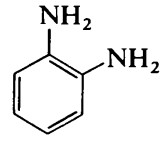


p-aminophenol

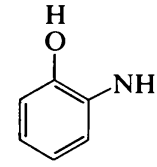
2. The two groups must be in the 1 and 2 (ortho) or the 1 and 4 (para) positions on the benzene ring but not in the 1 and 3 (meta) positions. Meta-substituted compounds do not form practical developing agents.[45] Replacement of the oxygen by sulfur in *p*-aminophenol destroyed its developing properties.[46] The three developing agents listed under (1) above are examples of para-substituted developing agents. Below are three examples of ortho-substituted developing compounds.



catechol

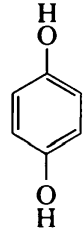


o-phenylenediamine



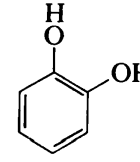
o-aminophenol

3. A developing agent is more powerful if its two groups are in the para arrangement than if they are in the ortho configuration.

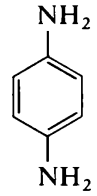


hydroquinone

is more powerful than

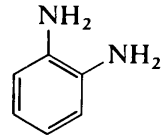


catechol

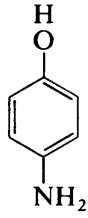


p-phenylenediamine

is more powerful than

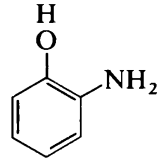


o-phenylenediamine



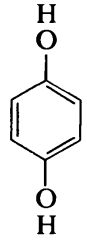
p-aminophenol

is more powerful than



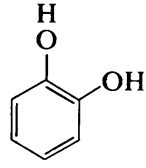
o-aminophenol

4. The benzene derivatives with two —OH groups are more active than those with one —OH and one —NH_2, and both of these types are of greater activity than those derivatives containing two —NH_2 groups.



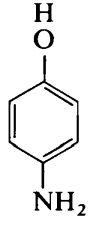
hydroquinone

and



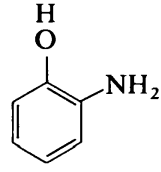
catechol

are more active than



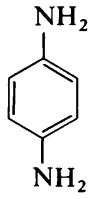
p-aminophenol

and



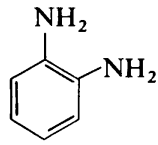
o-aminophenol

These compounds in turn are more active than



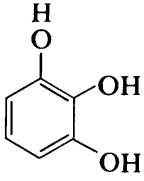
p-phenylenediamine

and



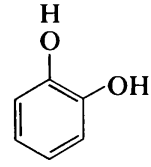
o-phenylenediamine

5. More than two —OH or —NH_2 groups on the ring do not reduce the developing activity of the compound and may considerably enhance it.

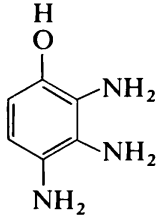


pyrogallol

is a more powerful developing agent than

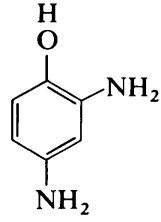


catechol



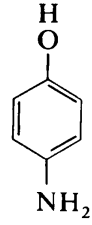
triaminophenol

is more active than



Amidol

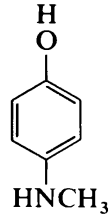
which is more active than



p-aminophenol

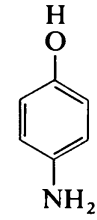
6. Replacing an —H of an —OH or —NH_2 group affects the developing properties of a compound. If the —H of an —OH is replaced by a —CH_3 or similar alkyl group, the developing activity of the compound is destroyed.

Substitution of an alkyl group for one or two of the —H's on the $—NH_2$ group will enhance the compound's reducing activity, but substitution of an acidic group (such as —COOH or $—SO_3H$) for an —H of an $—NH_2$ will lower the developing activity.



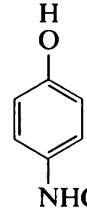
N-methyl-*p*-aminophenol

is more active than

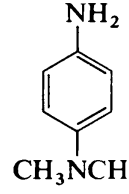


p-aminophenol

but both are more active than

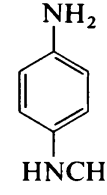


p-hydroxyphenyl-aminoacetic acid (Glycin)



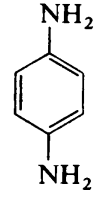
N,*N*-dimethyl-*p*-phenylenediamine

is more active than



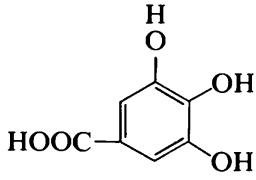
monomethyl-*p*-phenylenediamine

which is more active than



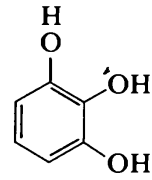
p-phenylenediamine

7. Substitution of an acid group (—COOH or —SO_3H) for an —H on the benzene ring lowers the developing energy of a developing agent; substitution of —Cl or —Br for an —H on the ring will enhance the activity. Substitution of an alkyl group, such as —CH_3, for a ring —H may enhance the developing action.

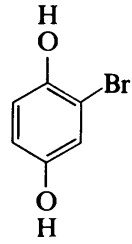


gallic acid

is less active than

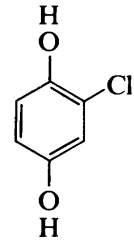


pyrogallol



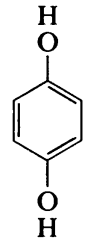
bromohydroquinone

is more active than



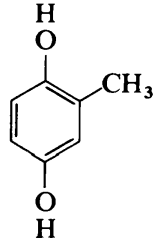
chlorohydroquinone

and both are more active than



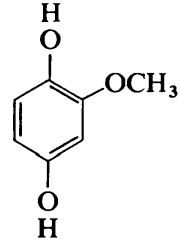
hydroquinone

Both



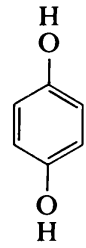
toluhydroquinone

and

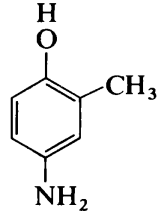


methoxyhydroquinone

are more powerful developing agents than

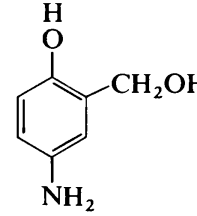


hydroquinone



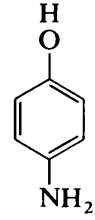
2-methyl-*p*-aminophenol

is more active than



2-hydroxymethyl-*p*-aminophenol

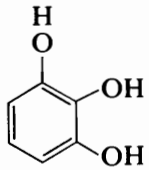
which is more active than



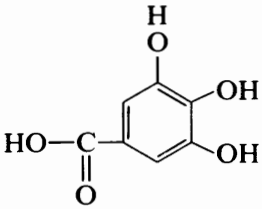
p-aminophenol

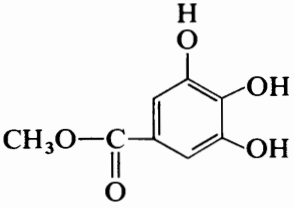
8. When only two —OH groups are present on the benzene ring, alkali is needed in the developing solution; when two $—NH_2$ or one $—NH_2$ and one —OH groups are present, the developing agent may act without alkali.[47,48] However, alkali will speed the activity of these developing agents.

9. A developing agent with three —OH groups (not a 1,3,5-substitution, which has no developing action) may act without alkali. A compound with three or more —OH or $—NH_2$ groups may be more active without alkali than with alkali present in the developing solution. The presence of a —COOH on the ring greatly weakens the developing activity, as with gallic acid or gentisic acid, but forming esters or acid amides restores much of the developing activity.[49,50]

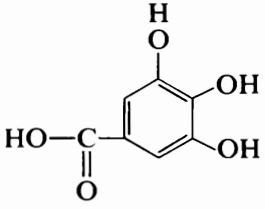

pyrogallol

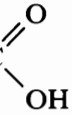
is much more active than


gallic acid

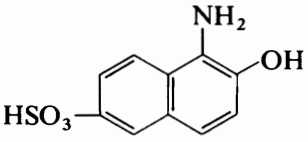

methyl gallate

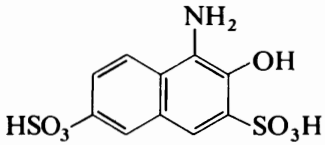
is much more active than

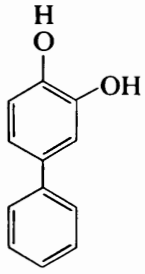

gallic acid

Substitution of $-CH_3$ or $-NH_2$ for the $-OH$ of the  produces developing agents of activity similar to pyrogallol.[51]

10. Compounds consisting of two fused benzene rings (napthalene) or two benzene rings bonded together (diphenyl) do not necessarily follow all of the rules for benzene compounds, but these two types of compounds do form active developing agents when two or more $-OH$ or $-NH_2$ groups are present on the rings. Often sulfonic acid groups ($-SO_3H$) are present to increase the solubility of the large developer molecules.

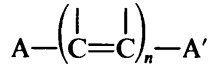

1-amino-2-naphthol -6-sulfonic acid [Eikonogen]


1-amino-2-napthol-3,6-disulfonic acid [Diogen]


4-phenyl catechol

Kendall Rule

By 1935 a number of organic developing agents had been found that were not derivatives of benzene or naphthalene. J. D. Kendall[52] proposed that these newer compounds, as well as the other developing agents, could be represented by a general formula:



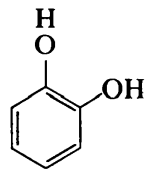
where A and A′ are either —OH, —NH_2, —NHR, or —NR_1R_2 groups and n is either zero or a whole number. The two unfilled bonds on the carbons are to be used to complete the structure of an organic molecule when n is 1 or greater.

When $n = 0$, the Kendall formula becomes A—A′; that is, the two functional groups are connected to each other without any intervening carbon atoms. Three simple possibilities exist:

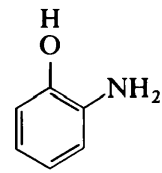
HO—OH	HO—NH_2	NH_2—NH_2
hydrogen peroxide	hydroxylamine	hydrazine

These compounds have found limited use in photography. Hydrogen peroxide is a weak developer at moderate solution alkalinities.[53,54] Hydroxylamine is an excellent developing agent at high pH, but it is relatively unstable, especially in the presence of metal ion impurities.[55] Hydrazine has a tendency to reduce unexposed as well as exposed silver halide.[56,57] To overcome these deficiencies many derivatives of hydroxylamine and hydrazine have been made by substituting carbon-containing groups for one or both of the hydrogens on the —NH_2 group.

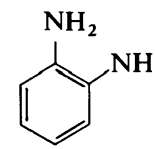
When $n = 1$, the Kendall rule becomes . This includes the ortho-substituted benzene compounds and derivatives:



catechol

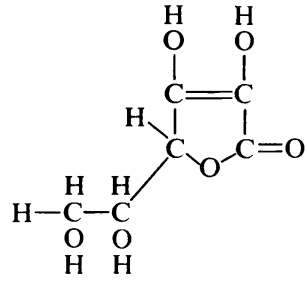


o-aminophenol

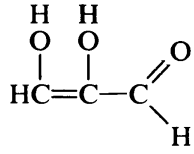


o-phenylenediamine

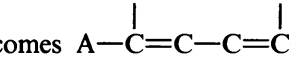
as well as nonbenzene compounds such as:

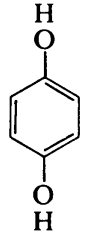


L-ascorbic acid

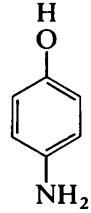


reductone

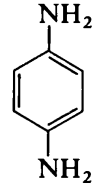
When $n = 2$, the Kendall rule becomes  This structure includes the para-substituted benzene and naphthalene developing compounds but not the corresponding meta-substituted compounds that are not developing agents.



hydroquinone

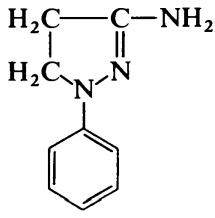


p-aminophenol



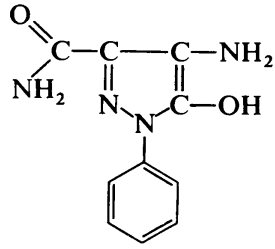
p-phenylenediamine

In 1940 J. D. Kendall found the developing agent called 1-phenyl-3-pyrazolidone. This compound, under its trademarked name Phenidone (Geigy Chemical Co.), has become one of the most important developing agents in use in modern photographic processing solutions. But Kendall's Phenidone does not conform to Kendall's own structural rule for developing agents. Compounds such as



1-phenyl-3-amino-pyrazoline[58]

and



1-phenyl-4-amino-pyrazolone-3-carboxylic acid amide[59]

also do not confirm to Kendall's rule. The Kendall rule was modified by W. Pelz[60] to

$$\gamma\text{—(A=B)}_x\text{—}\beta$$

which includes

$$\gamma\text{—}\left(\text{—}\overset{|}{\text{C}}\text{=}\overset{|}{\text{C}}\text{—}\right)_m\text{—}\beta \quad \text{and} \quad \gamma\text{—}\left(\text{—}\overset{|}{\text{C}}\text{=N—}\right)_m\text{—}\beta$$

where γ or β = —OH or NR_2 (R = —H or alkyl groups)

$$\text{A, B} = \text{—}\overset{\overset{|}{\text{R}}}{\text{C}}\text{=} \quad \text{or} \quad \text{—N=}$$

$$x = 0, 1, 2, \ldots.$$

The Pelz modification of the Kendall rule now covers Phenidone and other developing agents having nitrogen in the ring, but there are organic compounds of known developing action that are not covered by any structural classification. Formaldehyde, CH_2O, has been reported to be a developing agent. There are metal ions, such as iron, titanium, and vanadium, that are excellent developing agents in suitable solutions. Another inorganic developing agent, sodium hydrosulfite, $Na_2S_2O_4$, has been used to amplify latent images.[61,62] Although structural rules are useful in classifying developing agents, as are reduction potential measurements, there appears to be no structural rule that will include and identify all the possible compounds that are useful for the development of a latent image. Joseph S. Friedman[63] has noted that "There can be no adequate structural theory of developers, but there can be a resonance theory."

THE ELECTRONIC INTERPRETATION OF A DEVELOPING AGENT

Any substance that is capable of acting as a developing agent must be able to donate an electron or electrons to the silver halide grain. A metal ion gives up an electron, forming an ion with a more positive oxidation number. The reverse reaction occurs just about as easily. Other inorganic and organic molecules may also provide electrons, although the reaction may not be as easily reversible; but an organic molecule such as benzene, the parent molecule of so many developing agents, is relatively energy-poor and incapable of transferring an electron.

Benzene contains two kinds of electrons: sigma electrons and pi electrons. The sigma electrons form the electron pairs that form the single bonds between carbon atoms. These electron pairs are very tightly held between the

nuclei of the two carbon atoms. The pi electrons are farther removed from the nuclei of the carbon atoms and thus require less energy to escape. Pi electrons form the second electron pair of the second bond linking two carbon atoms. In benzene, the pi electrons tend to distribute themselves so that only one pi electron is associated with each carbon atom of the benzene ring. This electronic condition is sometimes represented by a hexagon with a circular swirl in the center. However, for the purpose of illustration in this book, the electronic condition of benzene is represented by a hexagon with alternating single and double bonds.

The distribution of the sigma and pi electrons of benzene makes a very stable electronic configuration. The molecule does not possess sufficient energy to transfer any of its electrons. However, if the electron density of the benzene ring could be increased, the loosely held pi electrons could become available for transfer to another atom or molecule. Replacing the hydrogens on the benzene ring with substituents containing oxygen and nitrogen may accomplish this. Certain substituents containing oxygen and nitrogen have electron pairs on the oxygen and nitrogen that are not used for bonding to other atoms. These free electron pairs are loosely bound to the atomic nuclei of the oxygen and nitrogen. These electrons are available for increasing the electron density of the benzene ring, converting the substituted benzene compound into a developing agent. Benzene is capable of acting as an electron donor when two or more substituents containing oxygen or nitrogen are substituted on the ring. These substituents are the —OH and $-NH_2$ groups listed in the Lumière–Andresen–Kendall–Pelz structural rules for the classification of a developing agent. The presence of nitrogen in a ring structure also provides sufficient electron mobility to produce developing agents.

The $-NH_2$ group $\left(\begin{matrix} H \\ :\ddot{N}:H \end{matrix}\right)$ has a solitary electron pair that is not used for bonding purposes; the —OH group ($:\ddot{O}:H$) has two pairs of such electrons; but the ionized hydroxy group ($-O^-$ or $:\ddot{O}:^-$) has three pairs. Hydroxy ions have a high electron density that permits a strong electron release to the benzene ring. Because the electron release is greatest with the ionized hydroxy groups, increasing the pH of a solution containing a benzene molecule with two hydroxy groups, ortho or para situated, increases the developing action of the molecule until both hydroxy groups are completely ionized. If the H of the hydroxy group is replaced with an alkyl group, such as $-CH_3$ in $-OCH_3$, then ionization cannot occur and the molecule does not act as a developing agent at all.

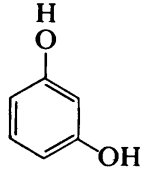
The $-NH_2$ groups do not need to be ionized to be electron-releasing, so these groups do not need the presence of alkali to make a benzene compound

act as a developing agent. But the electron contribution from an $—NH_2$ is smaller than from an ionized hydroxy group, making a developing agent with two $—NH_2$ groups located ortho or para on the benzene ring less active than a similar compound with two ionized hydroxy groups.

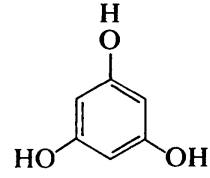
The substitution of a —Cl or —Br on the ring of a developing agent increases the activity of the developing agent. Both —Cl and —Br tend to give electrons to the ring, but this tendency is slight, owing to the nuclear attraction of these atoms for electrons. The introduction of a —COOH or $—SO_3H$ group for the hydrogen on an amino group results in a reduction of the activity of the developing compound. Both of these acidic substituents withdraw electrons from the benzene ring. The —COOH is especially electron-attracting. The resulting loss in electron density makes the compound less capable of being an electron donor. Pyrogallol consists of a benzene ring with three —OH groups in the 1, 2, and 3 positions. Pyrogallol is an active developing agent, but introducing a —COOH group on the ring, as in gallic acid, greatly reduces the developing action because of the electron-withdrawing action of the acidic group.

The electronic interpretation of the activity of developing agents offers a plausible explanation for the empirically derived structural rules of classifying developing agents. But a pure electronic interpretation fails to explain clearly why two, but not one, electron-releasing substituents are necessary, or why the two substituents must be ortho or para to each other, but not meta, for developing action to take place. Considerations other than electron release are necessary to characterize a developing agent. The formation of relatively stable intermediate oxidation products and their degree of adsorbability to the surface of the silver halide grain may also play a factor in determining the usefulness of a developing agent.

Benzene compounds containing electron-releasing groups in the 1, 3, and 5 positions do not act as developing agents of any significance. The structure of two such compounds is possessed by resorcinol and phloroglucinol.

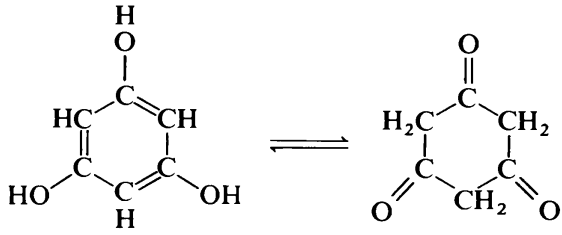


resorcinol



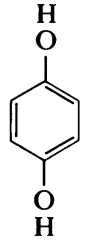
phloroglucinol

The failure of these compounds to act as developing agents has been attributed by B. Homolka[40] to an internal transformation that destroys the character of the electron-releasing groups attached to the ring. With phloroglucinol, this rearrangement has been proposed:

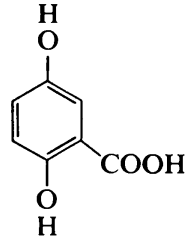


The electronic condition of the ring has been so altered that the molecule of phloroglucinol, or that of resorcinol, can no longer transfer electrons to the latent image. If $-CH_3$ groups replace the —H attached to the ring carbons, then the hydroxy groups are prevented from rearranging to form the double-bonded oxygens. The compounds containing the locked-in hydroxy groups were found to possess developing activity, thus supporting Homolka's hypothesis.

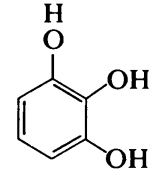
The introduction of the —COOH group on the ring of a developing agent, such as hydroquinone or pyrogallol, destroys almost all of the developing action of the compound under normal conditions.



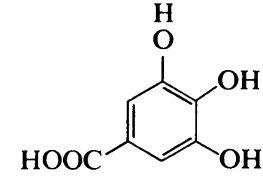
hydroquinone: a developing agent



gentisic acid: not a practical developing agent

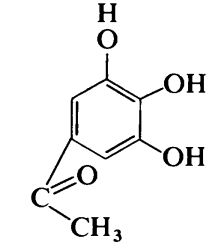


pyrogallol: a developing agent

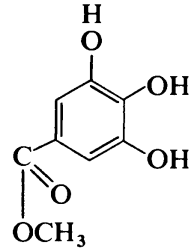


gallic acid: not a practical developing agent

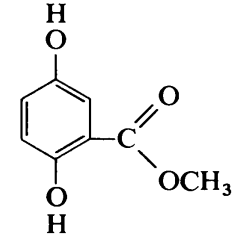
Yet closely related compounds such as



gallacetophenone



methyl ester of gallic acid



methyl ester of gentisic acid

are almost as active as the unsubstituted parent developing agent. Homolka[43] has shown that the acid function of the substitution cannot be the cause of the

loss of activity, as the corresponding stronger sulfonic acids (—SO_3H in place of the —COOH) are still active under normal developing conditions.

In a further study of this problem E. C. Armstrong, T. H. James, and A. Weissberger[51] concluded that di- and trihydroxybenzenes were inactivated by the introduction on the ring of —COOH (or —NO_2 as well) by forming ions that have the carbon or nitrogen of each group existing part time in a double-bonded form (=CO_2 or =NO_2). The presence of these forms paralyzed the activity of hydroxy groups in the ortho or para positions but not if the hydroxy was in the meta position. When the —COOH is modified, as in the ester of the acid, the molecular rearrangement cannot occur, and the compound is an active developing agent. The —SO_3H group cannot undergo this type of arrangement. Sulfonic acid derivatives are active developers.

In a more recent study T. H. James[50] has concluded that the slow developing rate of gallic acid and protocatechuic acid (the —COOH derivative of catechol) may be due to the high negative charge on the ions of these compounds in alkaline solution. In compounds where the acidic group is located ortho to a hydroxy group, as in gentisic acid and 2,3-dihydroxybenzoic acid, the lowered activity may be the result of the hydrogen bonding between the two adjacent groups. Such hydrogen bonding could decrease the ability of the compound to ionize, resulting in a loss of developing activity. The methyl esters of these two acids would not be capable of such an interaction with adjacent hydroxy groups, and the esters of these acids are more active developing agents.

The electronic structures of the substituted benzene developing agents have been studied by Tadaaki Tani.[64] He proposed the following general rules for developing agents:

I. The highest occupied electronic energy levels of developing agents are higher than those of nondeveloping agents.
II. The highest occupied orbitals of developing agents have antibonding nature, and those of nondeveloping agents have nonbonding or bonding nature.

Tani's findings provide the quantum-chemical explanation of the Kendall and Pelz rules of structure for developing agents.

OTHER CLASSIFICATION PROPOSALS

G. I. P. Levenson and T. H. James[65] state that "No single system completely specifies the properties of various agents," but later conclude that "A reasonably consistent account of the behavior of the various types of developing agents can be given on the basis of consideration of both ionic species and specific adsorption properties." An "electron-transfer" barrier has been

proposed by J. Q. Umberger[66] that limits the rate during the early stages of development.

A physical-chemical classification of developing agents has been proposed by Umberger[67] based on the principles of the chemistry of the free-radical forms of the agents. All of the common developing agents reduce exposed silver halide grains at different rates. These differences, according to Umberger, may be accounted for by three qualitative rules:

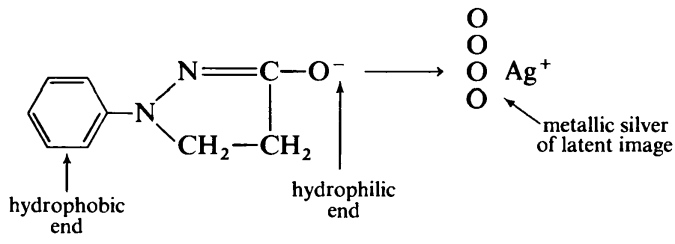
RULE 1 Proton loss precedes electron loss for active developing agents.

RULE 2 Electron loss should produce a resonance-stabilized free radical for active developing agents.

RULE 3 Developing agents readily losing two electrons per molecule tend to be catalyzed by oxidants.

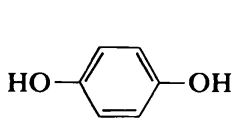
Development of a silver halide grain may occur when the developing agent transfers an electron to the metallic silver of the latent image that is positively charged by the presence of Ag^+ ions from the silver halide crystal. Such a mechanism requires that the developing agent be adsorbed to the metallic silver of the latent image. Developing agents have been classified by J. Q. Umberger[68] by their surfactant character. Surfactants usually consist of a large molecule that is relatively water insoluble (hydrophobic) except for one end, which has good water solubility. In water solution the molecule is soluble because of the water-soluble group—that is, because of the hydrophilic group. In many developing agents the —OH and $—NH_2$ groups are sufficient to keep the developer molecule in solution; but when such groups absorb to the latent image, the molecule is relatively hydrophobic, assuring good adsorption for the electron transfer. A symmetrical molecule such as hydroquinone has poor adsorption or surfactant properties because it has a hydrophilic group still in the water phase when it attempts to adsorb to the latent image. Catechol, with its two —OH's near one end of the benzene ring, is a faster developing agent than hydroquinone. Developer molecules having a hydrophobic part and a hydrophilic part of the molecule are much more strongly adsorbed and thus are much more efficient for electron transfer.

Phenidone, for example, has good surfactant properties:

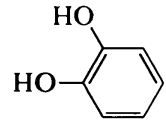


Phenidone has the phenyl group which is water insoluble and the ionized group which is water soluble. When the ionized group is attracted to positively charged metallic silver of the latent image, the rest of the molecule is forced from solution, causing Phenidone to have strong adsorption to the silver. The adsorption of Phenidone is so strong that bromide ions will be displaced, thus accounting for the ineffectiveness of bromide to interfere with Phenidone development.

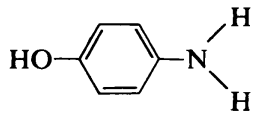
Converting a developing agent into a better surfactant will improve its electron-transfer capability and, hence, its ability to serve as a developing agent.



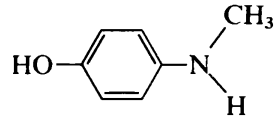
hydroquinone



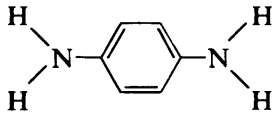
catechol



p-aminophenol

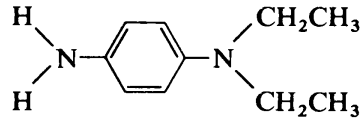


N-methyl-*p*-aminophenol



p-phenylenediamine

hydrophilic : hydrophilic



N,*N*-diethyl-*p*-phenylenediamine

hydrophilic : hydrophobic

PRACTICAL DEVELOPING AGENTS

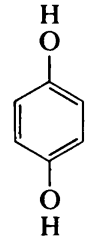
No one has ever attempted to list the many thousands of compounds that have been reported to be able to amplify the latent image. A considerable number of developing compounds have been listed in books by Pierre Glafkides,[69] C. E. K. Mees,[70] and Keith Henny and Beverly Dudley.[71] A great number of patents have been issued, but very few of these patented agents have ever been used commercially. As Mees has said, "The abundance of developing agents only increases the number of ways in which identical effects can be obtained."

The ability to amplify the latent image is not enough to make a developing agent into a practical compound of commercial importance. Other properties, such as solubility, stability in air and in solution, diffusibility through gelatin, toxicity to human beings, pollution of the environment, and cost of preparation, help determine the commercial introduction of a new developing agent. Actually, a potentially new agent should possess properties that are unique or in some way superior to those of developing agents already on the market.

Most modern developing solutions contain agents selected from about a dozen or so organic compounds. These practical developing agents range from pyrogallol (first used in 1850) to Phenidone (found in 1940 but not readily available until the early 1950s). Only two new developing agents of major importance, but of a different chemical structure, have been added to the list of useful black-and-white commercial agents in this century. The chemical structures of about a dozen agents provide a wide flexibility in the compounding of developing solutions of great variety. This number of compounds is sufficient to meet present-day solution needs, just as 88 keys on a piano are sufficient for playing fine music.

The individual properties of the widely used developing agents should be known. In the discussion that follows, the photographic properties of each developing agent are the properties of the single agent in solution. Such properties may vary widely, depending upon the alkalinity and other characteristics of the solution.

Hydroquinone (1,4-Dihydroxybenzene)

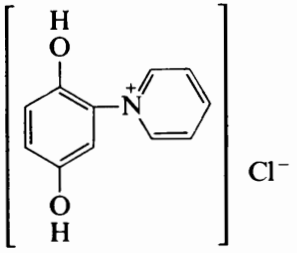


Hydroquinone, discovered by William de W. Abney[72] in 1880, is a developing agent in wide use today. As the sole developing agent this compound is slow to form an image but, once started, highly alkaline hydroquinone developers are capable of producing images of high contrast and high density.[73] Hydroquinone developers of high pH may be used for low-temperature processing, but development of some hydroquinone developers is slowed considerably by lower-than-normal temperatures. The oxidation products of

hydroquinone from the reduction of silver ions increase the rate of development. The oxidized products of hydroquinone development also react with gelatin to toughen it and reduce the solubility of gelatin in water. Such modification of the gelatin is called tanning.

A hydroquinone developer may produce a minimum of image detail in areas of low exposure of some photographic materials.[74] This tendency is increased by the presence of a bromide salt in the developing solution. To insure maximum development of weakly exposed areas, especially of bromide- containing photographic materials, another developing agent (such as Metol or Phenidone) is often combined with hydroquinone in the developing solution. The image resulting from the combined action of the two developing agents is superior to that of the sum of the actions of each agent used separately. The combination of hydroquinone with 6-amino-1,2,3,4-tetrahydroquinoline has been claimed to have a higher developing activity than hydroquinone-Metol developers and to be more stable in alkaline solutions than the combination of hydroquinone with Phenidone.[75]

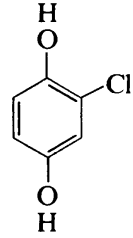
Some of the initial slowness in acting upon exposed silver halide by hydroquinone may be accounted for by the fact that the active species in development is the doubly charged ion.[76] This ion requires time to penetrate to the negatively charged silver halide crystal that repels it. The substitution of one or more positively charged substituents on the hydroquinone molecule has been found to shorten considerably the period before development begins.[77] Suitable substituents included the *N*,*N*-diethylaminomethyl- and *N*,*N*-di(β-hydroxyethyl)aminomethyl-groups located in the 2, or the 2 and 5 positions, of the hydroquinone molecule. K. Kumetat[78] introduced pyridine into the hydroquinone molecule, thereby adding a positively charged substituent.



Hydroquinone, in its active form for development, is hydrophilic in nature and is not easily adsorbed to the surface of the silver halide crystal. The hydroquinone ion can be made to leave the solution and become adsorbed by the addition of carbon chains to the ring of the hydroquinone molecule. J. F. Willems and G. F. van Veelen[79] have reported that "The developing activity of the alkylhydroquinones and the alkylhydroquinone sulfonic

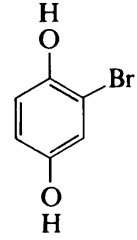
acids surprisingly increases quickly with growing length of the alkyl groups. Addition of 1-phenyl-3-pyrazolidinones practically eliminates all differences in developing activity in both series." Compounds such as methylhydroquinone or tertiary-butylhydroquinone are better developing agents than hydroquinone itself.

Chlorohydroquinone (2-Chloro-1,4-dihydroxybenzene)



Monochlorohydroquinone was introduced by Hauff in 1897. This compound has properties similar to those of hydroquinone but about six times greater developing energy. Its developing activity is said to resemble a developer containing hydroquinone with 5% Metol present. Chlorohydroquinone is extremely soluble in water, especially hot water, making possible its use in concentrated developing formulations. Chlorohydroquinone has also been used in developers designed to give warm image tones on photographic papers. This chloro derivative of hydroquinone has been marketed under the trade name of Adurol, but this trade name has also been used for bromohydroquinone.

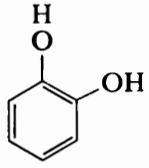
Bromohydroquinone (2-Bromo-1,4-dihydroxybenzene)



Monobromohydroquinone was introduced by Schering in 1897. It was called Adurol–Schering to distinguish it from Adurol–Hauff (monochlorohydroquinone).[80] The developing activity of bromohydroquinone was studied by M. Andresen in 1899.[81] The effect of various substituents on the hydroquinone ring upon developing activity was investigated by M.

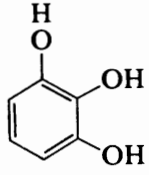
Andresen[82] and later by A. and L. Lumière and A. Seyewetz.[83,84] Substitution of the chlorine or bromine into the hydroquinone molecule increased its developing power. The presence of a sulfonic acid group (—SO_3H) decreased the activity, as did the presence of the nitro group (—NO_2). Two nitro groups completely destroyed the developing action. Bromohydroquinone was somewhat more energetic than chlorohydroquinone. The presence of the methyl group "very considerably increases the developing power of hydroquinone," according to the Lumières and Seyewetz.

Catechol (1,2-Dihydroxybenzene)



Catechol (sometimes called pyrocatechol or pyrocatechin), reported as a developing agent in 1880 by J. M. Eder and V. Tóth,[85] is closely related to hydroquinone in structure and resembles it in activity and sensitivity to bromide ions.[86] The univalent ion was found by T. H. James[87] to be the active form at the beginning of development. In the presence of low quantities of developer preservative, catechol produces a residual stain image in those areas where development has occurred. This stain image is effective in intensifying the lower image densities, making weak densities more effective. The oxidized product of catechol also tans gelatin in the image area. Catechol has been reported to be capable of image development even in the presence of considerable amounts of silver halide solvents, making this developing agent suitable for combined developing and fixing solutions.[88]

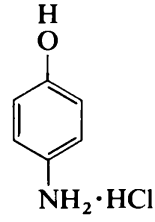
Pyrogallol (1,2,3-Trihydroxybenzene)



Pyrogallol, or pyro as it is often called, was first employed as a developing agent by Frederick Archer[89] in 1850 in the wet colloidion process. H. V. Regnault and J. Liebig used pyrogallol in 1851. This compound forms soft-working but rather slow-acting developers at moderate alkalinities. Chrome

alum or *p*-phenylenediamine has been proposed to activate or accelerate the rate of pyrogallol development.[90] In developers containing low concentrations of preservative, the oxidation products of pyrogallol development produce a residual yellowish-brown stain. This stain reinforces the silver image and is especially effective in obtaining maximum emulsion sensitivity and fine grain from the photographic material.[91] The oxidation products from pyrogallol development also tan the gelatin in the areas of image formation. Increasing the preservative in the developing solution inhibits the staining and tanning actions of the developer. But solutions of pyrogallol, even with preservative present, are very unstable in the presence of the oxygen of the air.[92,93] The working solutions of pyro developers are mixed just before use and discarded immediately after use. Because of its many desirable properties, pyrogallol has been combined with a number of other developing agents, especially to shorten the time of development of the rather slow-acting pyrogallol. Alkyl-substituted pyrogallols are claimed to have improved solution stability and to be free from a tendency to stain the hands.[94]

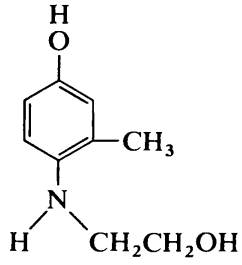
para-Aminophenol Hydrochloride (4-Aminophenol Hydrochloride)



para-Aminophenol was first used as a developing agent by Momme Andresen in 1888.[95] Both Andresen[96] and the Lumières[97] studied *p*-aminophenol developers in 1891. Because of the poor stability in air, this compound is commercially available as the more stable hydrochloride salt. The salt is considerably more soluble in water than is the free base. The free base, however, is very soluble in strong alkali, such as sodium hydroxide, forming the sodium phenolate salt. Concentrated developers of the Rodinal type are made by dissolving large quantities of *p*-aminophenol in caustic solution.[98,99] Developers containing *p*-aminophenol produce images free from stain with very low fog levels, even in highly alkaline solutions or at high temperatures.[100] Such developers are especially suitable for tropical development conditions or other high-temperature processing uses.[101] Developers containing *p*-aminophenol are resistant to aerial oxidation, but highly alkaline solutions do require a developer preservative to protect the developing agent. *p*-Aminophenol can be combined with hydroquinone to produce

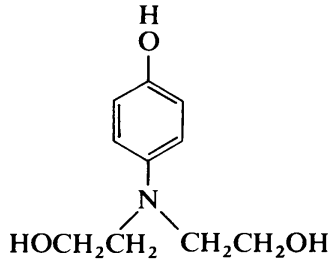
developing solutions that are adaptable to many uses and free from certain impurities that may cause skin allergies.[102,103]

The desirable developing action of *p*-aminophenol has led to the study of derivatives of this compound. The Lumière brothers and A. Seyewetz[104] found that alkyl groups, such as $-CH_3$, destroy developing activity when substituted for the —H of the —OH but yield good developing agents when substituted on the $-NH_2$ in place of one or two of the —H groups. One compound, *N*-methyl-*p*-aminophenol, is a widely used developing agent as the sulfate salt. This compound (Metol) is discussed separately in the next section. Other *N*-substituted *p*-aminophenols have been patented, such as:



4-(hydroxyethylamino)-3-methyl-1-hydroxybenzene[105]

or



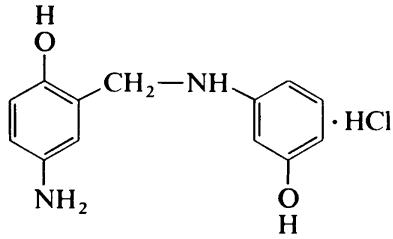
4-[di(hydroxyethyl)]amino-1-hydroxybenzene[106]

N-Methyl-para-amino-ortho-chlorophenol sulfate showed no advantage as a developing agent over *N*-methyl-*p*-aminophenol.[107]

ortho-Aminophenols, particularly the 2-hydroxyethylamino-1-hydroxybenzene, have been of interest since that compound was patented in 1927.[108,109] Fine-grain images are obtained when 2-hydroxyethylamino-1-hydroxybenzene is used as the sole developing agent, but the development time is longer than desirable. It is considerably shortened when para-hydroxyphenylaminoacetic acid (photographic Glycin) is also present in the solution.[110] There was no appreciable effect on the other characteristics of the developed image. The combination of *N*-monoethyl-ortho-aminophenol with 2-[di(hydroxyethyl)]amino-1-hydroxybenzene was claimed to give increased emulsion speed without any appreciable increase in grain.[111] The presence of iodide ions (0.1 to 0.4 g/liter of solution) in a developer containing *N*-(2-hydroxyethyl)-ortho-aminophenol was said to minimize changes in solution activity when the solution was used repeatedly without regeneration.[112]

Certain 2-substituted *p*-aminophenols have been patented[113,114] for their ability to act as a silver halide developer and as a color former to produce a dark brown or black dye. Such images of high density could allow less silver

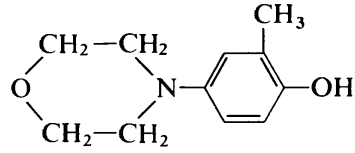
halide to be used in the photographic material and still obtain a satisfactory image. One such dye-forming developing agent had the structure:



N-(2′-hydroxy-5′-aminobenzyl)-
3-hydroxy-aniline hydrochloride

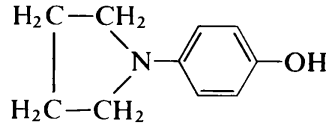
In some combined developer-fixers there is a loss of density due to the action of the fixing agent during development. The presence of the 2-substituted *p*-aminophenol developing agent and color former in a combined developer-fixer was said to prevent any loss in density, gradation, and sensitivity.[115] The dyes produced may be blackened and stabilized against pH effects by treatment with an alkaline solution containing a metal complex selected from the group consisting of copper, cobalt, nickel, cadmium, zinc, and silver.[116]

N,*N*-Disubstituted *p*-aminophenols have been said to have special developing properties. The compound



m-methyl-*p*-hydroxy-*N*-phenyl-morpholine

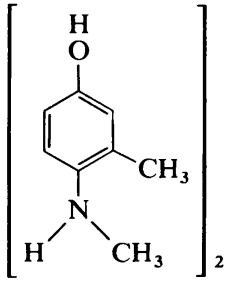
in a developing solution was claimed to correct the effects of improper exposure, good results being obtained with "somewhat under- or over-exposed" photographic materials.[117] A high degree of additive developing action resulted when hydroquinone and a *p*-aminophenol compound such as



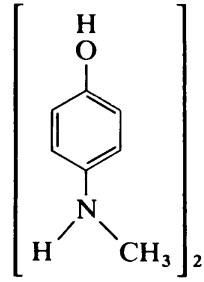
1-(4-hydroxyphenyl)-pyrrolidine

were present in the same developing solution.[118,119] 4-Hydroxy-3-methyl-*N*,*N*-diethylaniline hemisulfate was also an efficient compound to use with hydroquinone in developers.[120,121]

Metol (*N*-Methyl-para-aminophenol sulfate)



para-methylamino-meta-cresol sulfate (early Metol)



N-methyl-para-aminophenol sulfate (Metol or Elon)

In 1891 A. Bogisch found the developing action of Metol, which was introduced by Hauff.[122] The name has been said to be derived from *p*-METhylaminophenOL, but the early Metol was *p*-methyl-amino-meta-cresol sulfate.[123] In fact in 1907 Paul Hasluck's book, *The Book of Photography*, still identified the 3-methyl compound as Metol.[124] Present-day Metol does not have this methyl group; during wartime, however, Metol of the early structural form was used.

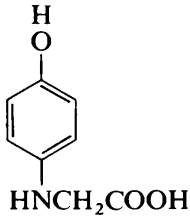
Metol forms soft-working developing solutions that are relatively unaffected by the presence of bromide ions. Metol solutions keep very well and do not stain gelatin or the hands of the photographer. This agent forms active developers in an aqueous sodium sulfite solution, but the Metol must be added to the water first. The free base of Metol is practically insoluble in concentrated sodium sulfite solutions. The low-contrast, fine-grain images produced by Metol development have good detail in areas of low exposure. Thus, Metol is often used in developing solutions compounded to give maximum emulsion speed of the photographic film material.

Metol is often combined with a contrast-building developing agent, such as hydroquinone, to produce energetic developers of good contrast and shadow detail.[125] The Metol-hydroquinone developer produces photographic results that are greater than the sum of the results given by the compounds used separately. In his study of the Elon-hydroquinone developer, Gerald I. P. Levenson[125] said, "While Elon yields rapidly acting developers and hydroquinone developers are slow to act, Elon-hydroquinone developers can act more rapidly, under suitable conditions, than Elon developers. The activity of a hydroquinone developer is greatly increased by the addition of a very small quantity of Elon."

Because of their additive properties, Metol and hydroquinone have been widely used in developers for almost every kind of photographic paper and

film—their solutions being referred to as MQ (Metol-Quinol) developers—(Quinol was an early commercial name for hydroquinone). MQ developers have been used for 80 years and continue to be an important part of modern photographic processing.[126]

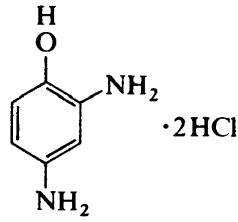
Glycin (para-Hydroxyphenylaminoacetic Acid)



Photographic Glycin, like Metol, was a discovery by A. Bogisch in 1891.[122] Metol was the result of a substitution of a $-CH_3$ for a hydrogen of the $-NH_2$ of para-aminophenol. Glycin resulted from a substitution of $-CH_2COOH$ for a hydrogen of the $-NH_2$ of para-aminophenol. Photographic Glycin should not be mistaken for the amino acid, glycine, NH_2CH_2COOH. The resulting acidic compound is only very slightly soluble in water but is soluble in alkaline solutions.[127] Glycin is added to a developing solution after the sodium sulfite has been added to give an aqueous solution of low alkalinity. Glycin developers can be made in concentrated form or used in two baths.[128]

Glycin developers are very resistant to aerial oxidation, nonstaining, fog-free, but very slow acting. They are very similar to hydroquinone developers in their sensitivity to soluble bromide in the developer. Glycin may be used as the sole developing agent, giving warm-toned images on certain photographic papers. Usually, Glycin is combined with another developing agent, such as para-phenylenediamine, to produce fine-grain developers of low energy.

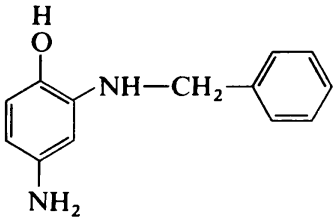
Amidol (2,4-Diaminophenol Dihydrochloride)



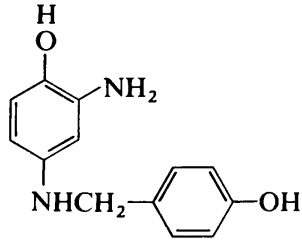
Amidol was discovered in 1891 by Momme Andresen (German Patent 60,174). This compound is *p*-aminophenol with an $-NH_2$ added in the 2-position of the benzene ring; this extra amino group greatly increases the developing energy of the compound. Amidol is so active that it will develop without alkali or even in acidic solution, though slowly.[129,130] In weakly alkaline solutions, such as those given by sodium sulfite, Amidol is an energetic developing agent.[131,132] Excess sodium sulfite was found to accelerate the oxidation of the Amidol in solution.[133] In alkaline solution, Amidol oxidizes rapidly; and many compounds, such as boric and lactic acid, have been suggested as additions to the solution to prevent the loss of the Amidol.[134,135] Developers containing Amidol produce rich black tones on photographic papers, but the developer must be prepared immediately before use. Amidol development has been recommended for black-and-white lantern slides[136,137] or for the correction of over- or underexposure.[138,139] Amidol is not appreciably affected by the presence of bromide ions, so that fog may be present with the low-contrast image given by some Amidol developers. Amidol and *p*-phenylenediamine have been used together in sodium bisulfite solution to produce a solution of good stability.[140]

According to the studies of Auguste and Louis Lumière,[141] substances with more than two —OH or $-NH_2$ on the benzene ring, but not the 1,3,5-configuration and not containing the —COOH group, are capable of acting as developing agents in neutral or even acidic solution. It was found that "A watery solution of amidol acquires notable developing powers as soon as sufficient sodium sulphite to saturate the hydrochloric acid contained in it is added and that notwithstanding the presence of the free sulphurous acid."[142,143]

One major disadvantage of developers containing Amidol is the lack of stability. The presence of stannic chloride in the developing solution has been reported to improve its keeping properties.[144] F. L. English[145] has found "Half a gram of stannous chloride ($SnCl_2 \cdot 2H_2O$) and an equal amount of tartaric acid dissolved in 10 cc of water added to one liter of standard developer will increase the keeping quality, under normal storage conditions, several hundred percent; and the further addition of a few pieces of mossy tin will prevent serious discoloration for a matter of months." Oxidized Amidol in solution has been found to produce a desensitizing substance that acts to keep the fog low during Amidol development.[146] Amidol produces a deeply colored oxidation product that can stain the hands or clothing of the person using it. Derivatives of Amidol that have improved solution stability and diminished staining tendencies are produced when one of the two $-NH_2$ groups has been substituted.[147] Examples of such developing agents are:

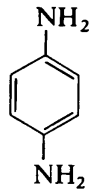


4-amino-2-benzylaminophenol



2-amino-4-(*p*-hydroxybenzyl-amino)-phenol

para-Phenylenediamine (1,4-Diaminobenzene)



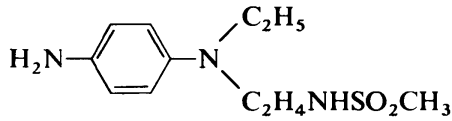
Momme Andresen described the developing action of *p*-phenylenediamine in 1888.[122] This compound has the lowest developing energy of all the practical developing agents in use today. This slow-reducing action gives extremely fine-grain silver images but with a considerable loss in emulsion speed of the photographic film. This loss is due in part to the solvent action upon silver halide by the diamine compound during the very long times needed for the development. Oxidation products of some *p*-phenylenediamines, such as 4-aminodiethyl-*m*-toluidine, retard development.[148]

Other developing agents, such as hydroquinone, Glycin, Metol, and Amidol, have been used with para-phenylenediamine to produce more energetic developing solutions. However, the developed images given by these developers are not as fine-grained as when the para-phenylenediamine is the sole developing agent. An exceptional developing activity has been found when quantities as small as 0.050 g of a tetra-alkylated *p*-phenylenediamine, such as *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine, is used in a liter of developing solution containing 5 g of hydroquinone.[149]

Although little used today for the developing of black-and-white films, para-phenylenediamine derivatives are the primary developing agents in color photography. After reducing the exposed silver halide of a color film, the derivatives of para-phenylenediamine form an oxidation product that reacts with color-forming organic compounds to form the dye images of color materials. Most color developing agents are *N*,*N*-dialkyl derivatives of

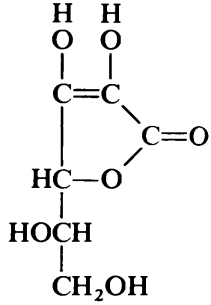
para-phenylenediamine, and such compounds have been studied in great detail.[150] The chemical constitution and reactions of these substituted para-phenylenediamines are described in detail in Chapters 9 and 10 of Volume 2 of this book.

p-Phenylenediamine and its derivatives produce allergenic reactions in some persons.[151] The oillike character of *p*-phenylenediamine and some of its derivatives allows it to penetrate the outer layers of human skin. Making the molecule more water soluble is claimed to make the compound less toxic. One method has been to attach the water-solubilizing group on the alkyl group attached to the nitrogen of the amino group,[152] such as in

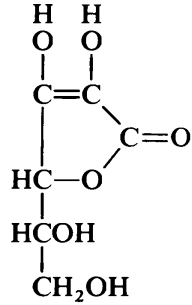


N-ethyl-*N*-(β-methanesulphonamidoethyl)-4-aminoaniline

L-Ascorbic Acid (Vitamin C) (Hexuronic Acid)



L-ascorbic acid

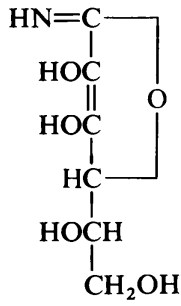


isoascorbic acid

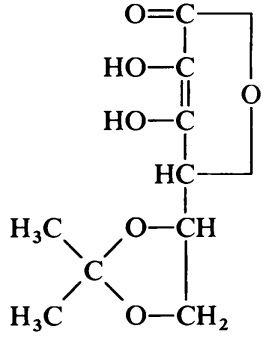
The study of the antiscorbutic properties of vitamin C revealed that this compound (ascorbic acid) had outstanding reducing properties.[153,154] Its ability to reduce silver ions was patented by Heinz Ohle[155] in 1932, but Charles E. Bills[156] claimed to have used ascorbic acid as a developing agent in 1931. In 1935 Kurt Maurer and G. Zapf[157] used isoascorbic acid and J. Rzymkowski[158] used sodium isoascorbate as developing agents. Isoascorbic acid has only about one-twentieth the biological activity of vitamin C.[159] Unlike most of the important developing agents of that time, which were benzene derivatives, the ascorbic acids were sugar derivatives.

Ascorbic acid, like hydroquinone, is a developing agent acting more vigorously at the higher solution alkalinities, also slow to get started but giving images with low fog.[160] Ascorbic acid forms very active developing

solutions when used in combination with Metol or Phenidone.[161,162] Developing solutions containing ascorbic acid are subject to oxidation, possibly because of the catalytic effect of metal ions such as copper.[163] Imino-L-ascorbic acid



and related sugar analogs are very weak developing agents by themselves in developing solutions; when combined with 3-pyrazolidones, such as Phenidone, developing solutions of much greater activity are obtained that are more active than the summing of the individual activities.[164] 5,6-Substituted ascorbic acids, such as 5,6-isopropylidene ascorbic acid,

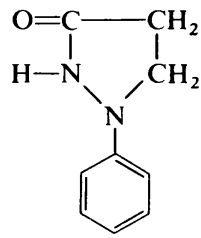


have been patented as active developing agents.[165]

The use of sugars, treated with alkalis, began long before the use of ascorbic acid. Maxwell Lyte[166] proposed in 1855 to use glucose (grape sugar) and lime, neutralized after several days with sulfuric acid, as a developing solution. Reductone made by heating glucose in sodium carbonate monohydrate for 2.5 min at 91 to 93°C was described as a photographic developer by Olus J. Stewart.[167] Combining reductones and 3-pyrazolidones in developing solutions has been patented.[168] Low stain and improved stability have been claimed for developers containing anhydro dihydro piperidino hexose reductone.[169] 4-Phenyl-2-oxytetronic acid and other 4-aryl-2-oxytetronic acids were claimed as developing agents that act more rapidly than ascorbic

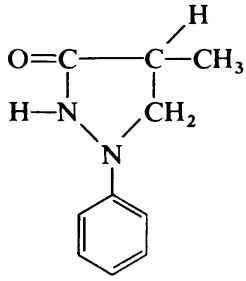
acid.[170] Dihydroxyfurans are active developing agents but have low stability in alkaline solution.[171]

Phenidone (1-Phenyl-3-pyrazolidone)

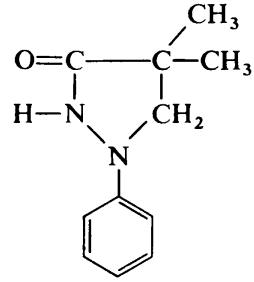


J. D. Kendall[172,173] found the developing action of 1-phenyl-3-pyrazolidone in 1940, but the compound did not become available until the early 1950s.[174,175] The commercial production of Phenidone was dependent upon a suitable method of manufacture, as the compound had been prepared as early as 1890.[176–179] 1-**PHEN**yl-3-pyrazol**IDONE** is a slow developing agent at low alkalinity, capable of acting as the uncharged molecule. Image detail in areas of low exposure is excellent, thus insuring good emulsion speed of the photographic material. The reducing action is little affected by the presence of bromide, so organic compounds called antifoggants are often added as fog restrainers to Phenidone developers. Benzotriazole has been reported to be more effective than potassium bromide as a fog restrainer.[180].

Phenidone is rarely used as the sole developing agent but is often combined with hydroquinone to secure adequate image contrast and density. Phenidone-hydroquinone (**Q**uinol)—that is, PQ—developers are similar to MQ (**M**etol-**Q**uinol) developers, but much less Phenidone than Metol is needed to secure equal activity. PQ developers have been formulated for many uses.[181–184] These low-staining developers avoid most of the allergenic reactions that some persons encounter when using Metol or the *p*-phenylenediamines.[185]



Methyl Phenidone



Dimezone

The 4-methyl derivative of Phenidone, called Phenidone B or sometimes Methyl Phenidone, and 4,4-**DIME**thyl-1-phenyl-3-pyra**Z**olid**ONE**, called Dimezone or dimethyl Phenidone, have found use in commercial developing solutions. Both of these methylated Phenidone derivatives are more stable than Phenidone in concentrated liquid developing compositions that may be maintained at high temperatures or may be stored for long periods of time.[186]

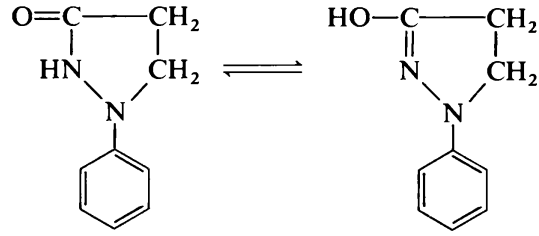
A large number of 3-pyrazolidone derivatives have been described.[187,188] The substitution of a methyl group in the 2 position destroys the developing activity of the molecule but 2 substitutions, such as hydroxymethyl or hydroxyethyl, produced developing agents of increased solubility.[189] 5-Methyl-1-phenyl-3-pyrazolidone is an active developing agent. Heterocyclic substituents in the 5 position of the 3-pyrazolidone ring have been patented.[190] 1-(*p*-Tolyl)-4,4-dimethyl-5-methoxy-3-pyrazolidone and related compounds have been prepared.[191]

The great value of Phenidone and its derivatives lies in the cooperative action that these compounds exhibit with certain other developing agents. This joint activity is called superadditivity of development, producing more density jointly than the sum of the densities produced by each developing agent separately under the same developing conditions. The lower the pH and the larger the amount of exposure, the more important is the dependence on the superadditive effect of pyrazolidones.[192] V. L. Abritalin et al.[193] reported that "The degree of superadditivity (SA) of twenty 3-pyrazolidone derivatives has been investigated during black-and-white development. It has been determined that the superadditivity of 3-pyrazolidone derivatives appears with hydroxybenzenes. The highest effect is reached for the *p*-derivative (hydroquinone). Aminophenols and phenylenediamines, except glycin, show no superadditivity with 3-pyrazolidone derivatives." When *p*-aminophenol contained a negatively charged group, such as a sulfonic acid group, superadditivity with Phenidone was reported by G. F. van Veelen and J. F. Willems.[194]

Abritalin et al.[195] investigated the superadditivity effect for hydroquinone with twenty 3-pyrazolidone derivatives and Metol. They found that "Of the 20 investigated pyrazolidone-3 derivatives, two derivatives, 1-(*m*-tolyl)- and 1-(*p*-tolyl)-pyrazolidone-3 have a greater superadditive effect than Phenidone; derivatives of 1-phenyl-5-methylpyrazolidone-3, 1-phenyl-5,5-dimethylpyrazolidone-3, acid chloride of 4'-sulfonic acid of 1,5-diphenyl-pyrazolidone-3 and the barium salt of the disulfonic acid of 1,5-diphenyl-pyrazolidone-3 are very close to Metol as far as the superadditivity of the developing effect is concerned; 1-(*p*-carboxyphenyl)-pyrazolidone-3 is worse than Metol as far as the superadditivity of the developing effect is concerned."

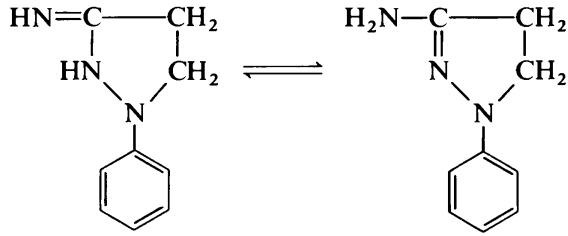
The superadditivity in photographic development of various substituted hydroquinones with Phenidone was studied by W. E. Lee and T. H. James,[196] who found that superadditivity did not correlate well with the nature of the substituents. Hydroquinone monosulfonate, according to A. J. Axford,[197] showed a marked superadditivity with Phenidone. Phenidone or other 3-pyrazolidones have been reported to show superadditive effects with gallic acid,[198] pyrogallol,[199] resorcinol,[200] or Glycin.[201] Two compounds, *N*-(4-hydroxyphenyl)-tetrahydropyrrole or *N*-(4-hydroxy-3-methyl-phenyl)-tetrahydropyrrole, each as the naphthalene disulfonate salt, have been claimed to be superior to Phenidone when used in combination with hydroquinone.[202]

3-Aminopyrazolines



1-phenyl-3-pyrazolidone | 1-phenyl-3-hydroxypyrazoline

1-Phenyl-3-pyrazolidone (Phenidone) can exist in the two forms shown above. In the preparation of Phenidone, an intermediate is used that has a =NH in the 3 position.[203,204] This compound, 1-phenyl-3-aminopyrazoline, may also exist in the two forms shown below.



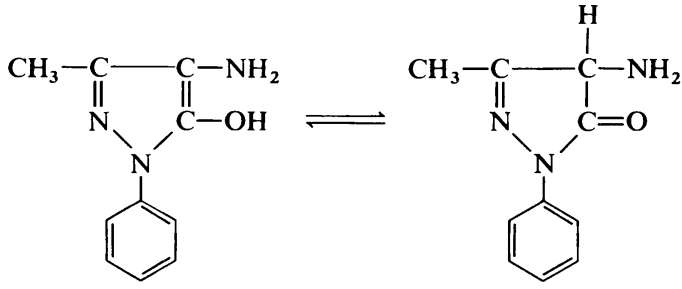
1-phenyl-3-pyrazolidone-imide | 1-phenyl-3-aminopyrazoline

This compound, unlike Phenidone, is without practical developing activity, even though there is a structural relationship between the 3-pyrazolidones and the 3-aminopyrazolines. It has been found, however, that active developing agents are produced when the 3-aminopyrazoline has substitutions in

the phenyl ring. Such substitutions may include halogen, or an alkyl, alkoxy, hydroxy, amino, acylamino, alkylamino, or acid groups.[205] Particularly effective are compounds with —OH or —NH_2 groups in the 4 position of the phenyl group.[206,207] Examples of such compounds are 1-(*p*-hydroxyphenyl)-3-aminopyrazoline or 1-(*p*-aminophenyl)3-aminopyrazoline. These compounds have been patented for use in combined developing and fixing solutions as well.[208]

1-(*p*-Aminophenyl)-3-aminopyrazoline has a pronounced superadditivity with hydroquinone. H. Ulrich and H. Schueler[209] found that "Developers containing the 3-aminopyrazoline derivatives have a shorter induction period, and lower concentrations of the agent are required for maximum superadditivity" than for similar hydroquinone developers that contained 1-phenyl-3-pyrazolidone. No superadditive effect was shown by 1-(*p*-aminophenyl)-3-aminopyrazoline with Amidol, Metol, Phenidone, or methyl Phenidone, or 1-(*m*-tolyl)-3-pyrazolidone, but an appreciable effect was obtained with Glycin, hydroquinone or chlorohydroquinone, or pyrogallol.[210] Superadditivity was found to be dependent upon the structure of the 3-aminopyrazoline and the black-and-white developing agent. Electropositive groups on the phenyl group and hydroquinone, respectively, were best. The 3-aminopyrazolines with electropositive groups on the phenyl were as good in their activating action as Phenidone but required smaller quantities of compound and were more soluble.

4-Amino-5-Pyrazolones



1-phenyl-3-methyl
4-amino-5-pyrazolone

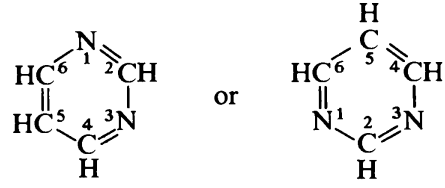
The developing activity of 1-phenyl-3-methyl-4-amino-5-pyrazolone was known as early as 1935 when I. G. Farbenindustrie applied for a British patent.[211] As shown above, the 4-amino-5-pyrazolones have a structural relationship with the 3-aminopyrazolines and the 3-pyrazolidones. Possibly because of this resemblance, the 4-amino-5-pyrazolones have been studied more thoroughly in recent times. Active developing agents were said to result

when alkyl, alkoxy, hydroxy, amino or substituted amino, or carboxyl or sulfonic acid groups were substituted on the benzene nucleus of 1-phenyl-3-methyl-4-amino-5-pyrazolone.[212] The presence of Phenidone, Metol, or 1-(*p*-aminophenyl)-3-aminopyrazoline in developing solutions containing 4-amino-5-pyrazolones and hydroquinone was patented as a means of improving the aeration stability of the solution.[213]

The development characteristics of 4-amino-5-pyrazolone developers have been thoroughly studied. 1-Phenyl-3-methyl-4-amino-5-pyrazolone develops over the pH range from 5 to 10 with only a short induction period.[214] At high exposure levels the maximum rate of development is reached at pH 8 or lower; at low exposure levels the development rate increases with pH but fog rises rapidly in alkaline solutions. Substitution of esters or amides of an acid group in the 3 position, as in 1-phenyl-4-amino-5-pyrazolone-3-carboxamide, produced developing solutions that were little influenced by the pH in the region from 7 to 10. Superadditivity with hydroquinone is shown.[215,216]

The effect of various substituents on the 1-phenyl group of 1-phenyl-3-methyl-4-amino-5-pyrazolone has been determined.[217] The presence of a sulfonic acid decreased the rate of development. Methyl or methoxy groups decreased the selectivity of development; chlorine atoms increased greatly the selectivity. 1-Chlorophenyl-3-methyl-4-amino-5-pyrazolone was said to show more selectivity than Amidol and to match it in development speed.[218] T. I. Krestovnikova et al.[219] found that most of the 4-amino-5-pyrazolones in hydroquinone solutions had a superadditive developing effect for the visible spectral region of exposure, although the effect was less than with Metol. A subadditive effect was found for the ultraviolet spectral region.

Pyrimidine Developing Agents

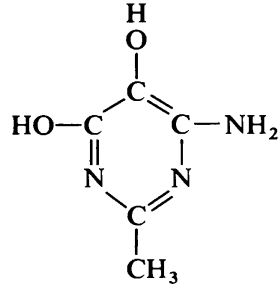


The six-membered pyrimidine ring is similar to a benzene ring in which two carbons (at the 1 and 3 positions) have been replaced by nitrogen atoms. The pyrimidine ring may be written in either of the two forms shown above, and the numbering of the atoms in the ring is indicated. Pyrimidine rings become developing agents when amino, hydroxy, and methyl groups are

attached to the ring carbon atoms. A 1938 patent[220] claimed fine-grain development was possible when the ring of the pyrimidine had amino or hydroxy groups in the 2- and 5-positions. The patent also indicated that the pyrimidine developing agent could be incorporated into the emulsion layer, or an adjacent layer, of the photographic material so that development could be carried out in an alkaline solution.

The reducing action of 26 pyrimidines was studied by E. B. Knott.[221] He used pyrimidine rings substituted with amino or hydroxy groups in the 5 position and with amino, hydroxy, or mercapto groups in the 2 position. R. W. Henn and Sue V. Carpenter[222] studied pyrimidines substituted by two or more adjacent amino and hydroxy groups. They found that "Further substitution by methyl groups or additional functional groups increased activity. The amino-substituted agents were more active than those containing only hydroxy groups, which were very pH dependent. Activity was increased by combination with hydroquinone or 1-phenyl-3-pyrazolidone. However, the activity of the combinations was lower than that of Elon-hydroquinone and they gave less emulsion speed and more fog. Two of the agents were oxidized with silver ammonium nitrate and found to form two atoms of silver per mole of developing agent."

The good developing activity and low level of stain of the oxidized form suggested to Edwin B. Wyand and William C. Farley[223,224] the use of the 5-hydroxy and/or 5-amino pyrimidines as developing agents for in-camera production of black-and-white prints. An example of such an active, low-staining pyrimidine developing agent is



4-amino-5,6-dihydroxy-2-methyl pyrimidine

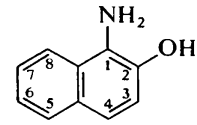
These pyrimidine developing agents "can be used in combination with other photographic developing agents, such as reductone developing agents, aminomethyl hydroquinone developing agents, cinnamic acid developing agents, lactone developing agents, or developing agent precursors, e.g., coumarin developing agents or developing agent precursors."

Naphthalene Developing Agents

In German Patent 50,265 Momme Andresen claimed the use of diaminonaphthalene sulfonic acids and aminonaphthol sulfonic acids as photographic developing agents. The dihydroxynaphthalenes, with or without sulfonic acid substituents, were also patented as developing agents.[225] Andresen gave the name "Eikonogen" to the compound, 1-amino-2-naphthol-6-sulfonic acid, which had been prepared by Raphael Meldola in 1881.[226] Eikonogen was marketed by Hauff and became popular as a replacement for the pyrogallol developer.[227]

R. B. Forster and H. T. Hanson[228] investigated the relationship of structure to the photographic developing properties of the following types of naphthalene compounds:

1. 1-Amino-2-hydroxy (shown at right).
2. 2-Amino-1-hydroxy.
3. 1-Amino-4-hydroxy.
4. 1,2-, 1,4-, and 1,5-Diamines.
5. Amino and hydroxyl groups in different rings.
6. Two hydroxyl groups and no amino group.
7. 1,2-Diamines with a hydroxyl group in the other ring.
8. 2-Amino-1-hydroxy compounds with a second amino group in the other ring.
9. 1-Amino-2-naphthol-3-carboxylic acid.



The effect of the substitution of one or more sulfonic acids on either ring of naphthalene was also studied for the influence on the developing action of the molecule.

Forster and Hanson found, in part, that

The 1-amino-2-hydroxy compounds appear to possess the developing function to the most marked degree. The introduction of a sulphonic acid group is an advantage as it increases the solubility of the compound. Its position is also of importance, the developer being most vigorous when it is in the 8-position and least vigorous in the 4-position. It has a marked effect on the stability, for while 1-amino-2-naphthol-8-sulphonic acid oxidizes very easily, 1-amino-2-naphthol-4-sulphonic acid is comparatively stable. The introduction of a second sulphonic group appears to retard the developing activity (cp. action without alkali).

The introduction of the sulphonic acid group into 1-amino-4-naphthol increases the developing activity considerably, the amino-naphthol being a weak developer and its 8-sulphonic a strong developer.

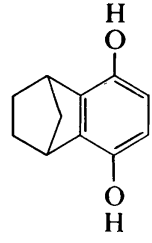
1 : 2- and 1 : 4-Diaminonaphthalenes are active developers; whereas the 1 : 5-compound has no developing function. When a sulphonic acid group is introduced into the 1:2-

diaminonaphthalene nucleus, the developing function is destroyed; in the case of the 1:4- compound, however, the 6-sulphonic acid is a strong developer, while the 8-sulphonic acid is much less active.

An alkaline solution of α-naphthol was found to give a color image on a silver bromide plate.[229] V. I. Zakharov, N. R. Novikova, and N. A. Perfilov concluded that "the image obtained after developing the material in α-naphthol is 'a matrix' of an ox-form of α-naphthol in the form of a tape and spherical silver grains distributed in the tape." The compound, 4-methoxy-1-naphthol, is known to develop a silver image and a blue dye image at the same time. In the case of British Patent 1,122,085[230] 4-methoxy-1-naphthol was used with Phenidone to form a more stable developing solution, because more developer preservative (sodium sulfite) may be present in the solution than when Phenidone is not present. Blue-black dye plus silver images have been reported when sulfonic acid derivatives of naphthalene developing agents were used to develop latent photographic images.[231] The dye may be used to reinforce the silver image, offering the possiblity of requiring less silver halide in the light-sensitive photographic material. Such a reduction of silver would be most beneficial with X-ray photographic materials, and the blue-colored image of the processed material would not be a disadvantage.

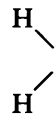
Naphthalene derivatives have been proposed to form black dye silver images from which all the silver has been removed.[232] In this case, however, a compound such as *p*-nitrobenzoyl-acetic-5-hydroxynaphthylamide was incorporated in the silver halide layer and the image developed in a color-forming developer, such as one containing *p*-diethylaminoaniline.

Bridged polyhydroxynaphthalenes have been incorporated in gelatin silver halide layers.[233] During development, the oxidation product of this developing agent reacts with the gelatin to make it less soluble, hardening or tanning the gelatin where development occurred. The unhardened gelatin may then be washed away, leaving a relief gelatin image. A suitable bridged polyhydroxynaphthalene for this purpose was 5,8-methano-5,6,7,8-tetrahydro-1,4-dihydroxynaphthalene:



This compound is also known as 3,6-dihydroxybenzonorbornane.

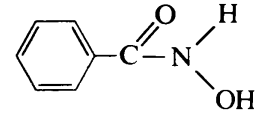
Hydroxylamine Developing Agents

The developing activity of hydroxylamine,  , was reported by Carl Egli and Arnold Spiller in 1884.[234] This simple molecule has been used by a number of investigators to study the reduction of silver salts. S. E. Sheppard and C. E. K. Mees[235] found that the reducing action of hydroxylamine was greatly accelerated by alkali. They found that "At moderate dilutions we have from the equilibrium $NH_2OH + NaOH \rightleftarrows NH_2ONa + H_2O$ the ion NH_2O^- which reacts with silver ions according to the equation:

$$2NH_2O^- + 2Ag^+ = 2Ag + N_2 + 2H_2O."$$

The result of development with hydroxylamine is nitrogen and water besides metallic silver. According to M. L. Nichols,[236] nitrogen was the sole gaseous product from the reduction of ammoniacal silver nitrate by hydroxylamine, but alkaline silver nitrate in the presence of sodium sulfite produced a mixture of nitrous oxide and nitrogen. T. H. James[237] said his results indicated that the hydroxylamine was adsorbed to the silver by means of the amino group. The active form of the reducing agent was the NH_2O^- ion. Only nitrogen was evolved.

Although hydroxylamine may have been of interest for development studies, the compound is not stable enough for practical developers. Hydroxylamine is usually now sold as an acid salt, usually the hydrochloride or the sulfate, but the oxalate salt was patented by Nathan Sulzberger in 1921.[238] One, two, or three of the hydrogen atoms of NH_2OH have been replaced by $—SO_3H$ groups, or a hydrogen atom may be replaced by a radical such as to form hydroxamic acid.[239]



The Lumière brothers and A. Seyewetz had studied the developing activity of hydroxylamine with a hydrogen replaced by a phenyl or tolyl group as early as 1894.[240,241]

The freedom from staining oxidation products has caused a current surge of interest in substituted hydroxylamines for in-camera instant picture processes. Edwin H. Land et al.[242–244] have patented alkyl-substituted hydroxylamines, such as *N*,*N*-diethylhydroxylamine, for developing agents, or other

hydroxylamines as aids in the image-forming process. Alkoxy hydroxylamines, as for example, *N*,*N*-di-(2-ethoxyethyl)-hydroxylamine, have also been patented.[245] The presence of 1,1-dimethylhydrazine was said to prevent aerial oxidation of this developing agent. Hydroxylamines containing an intralinear amino nitrogen (—N—) atom in the alkyl group attached to the nitrogen of the hydroxylamine[246] or one or two intralinear sulfone groups (—SO_2—)[247,248] were claimed to be more rapid acting and to have less odor than *N*,*N*-diethylhydroxylamine. Heterocyclic *N*-hydroxylamines—that is, the nitrogen atom of the hydroxylamine as part of a ring—are said to be "colorless, stain free, stable and relatively nonvolatile, especially in the salt form, and give black silver deposits on development."[249] Preferred heterocyclic *N*-hydroxylamines were *N*-hydroxy morpholine, *N*-hydroxy piperidine, and *N*-hydroxy pyrrolidine, and their salts, such as the oxalate.

Hydroxylamine and its derivatives have been patented[250,251] for superadditive developing combinations with *N*,*N*-disubstituted *p*-phenylenediamines, or with various 1,2,3,4-tetrahydroquinolines. Certain 6-amino- or 8-hydroxy-1,2,3,4-tetrahydroquinolines, either alone or in combination with polyphenols, *p*-aminophenols, or *p*-phenylenediamines have been patented.[252,253] Various 1-substituted-2-pyridone azines[254] and 1-phenyl-3-pyrazolidones[255] were also claimed to form superadditive combinations with hydroxylamine and its derivatives.

Hydrazine Developing Agents

The use of hydrazine, $NH_2—NH_2$, as a developing agent was an early photographic discovery. Emil Jacobsen patented substituted hydrazines in 1885.[256] Jacobsen found the developing properties of phenylhydrazine hydrochloride, —$NHNH_2 \cdot HCl$, a compound that was produced commercially in 1886.[257] Emil Votoček[258,259] experimented with a variety of substituted hydrazines. He found that "generally compounds which contain the hydrazine group possess developing properties and that even hydrazobenzole which may be considered asymmetric diphenyl-diamine possesses weak developing power. He also found that the sulpho group exerted no prejudicial action; and this is of importance, as most of the hydrazines are insoluble in water, whilst the corresponding sulphonic acids form salts readily soluble in water." The sodium bisulfite salt of phenylhydrazine was claimed by William Hay Caldwell[260] to produce a slow-acting developing solution of improved selectivity.

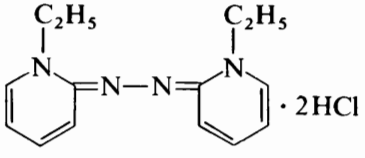
Hydrazine and its derivatives have not found important use as developing agents, possibly because of their toxicity, tendency to fog, and the low

solubility of some of the derivatives. Although the introduction of sulfonic acid or sulfonate groups, or carboxylic acid or carboxylate groups, into hydrazines does improve their solubility, these solubilized compounds do have less developing power. Primary aromatic hydrazines may be solubilized, according to James Emory Kirby,[261] in a solution of a long-chain, preferably 12 to 18 carbon atoms, carboxylic or sulfonic acid, and their salts. For example, phenylhydrazine formed a clear and colorless solution in a dilute aqueous solution of sodium oleate—0.1 to 1.0%.

Hydrazine or hydrazine derivatives have often been added to solutions containing other developing agents. The speed of a photographic emulsion was increased when hydrazine or hydrazine derivatives were present in a hydroquinone or Metol-hydroquinone developer.[262] Grant M. Haist and Harold D. Russell[263] "found that the development activity of hydrazine-containing developers, particularly when they are used for the development of direct positive images in an exposed internal latent image emulsion, is appreciably accelerated and the useful life of the developer composition is materially extended if certain quaternary ammonium compounds are incorporated into the hydrazine-containing developer." Examples of such quaternary ammonium compounds were 1-β-phenethylquinolinium bromide or β-phenylethyl-α-picolinium bromide.

Improved solubility and low propensity for staining were claimed for hydroxy-substituted aliphatic carboxylic acid aryl hydrazides, as patented by Ismael Adolfo Olivares, Frederic Roland Bean, and Grant Milford Haist.[264] These hydrazides, of which 2,2,2-tris(hydroxymethyl)acetyl-β-phenylhydrazide is an example, were said to be so substantially free from staining that the developing agents need not be washed from the emulsion layer after processing. When incorporated in the emulsion layer, the phenyl hydrazides could be activated by heat alone to produce a high-density image.

Superadditivity of development was obtained when a bis (pyridone)azine, such as 1-ethyl-2-pyridone azine dihydrochloride,



was combined in a developing solution with hydroquinone, a derivative of hydroquinone, or ascorbic acid. [265] The substitution of other heterocyclic rings for one hydrogen of each of the hydrazine nitrogen atoms has also produced developing agents that are superadditive with hydroquinone, chlorohydroquinone, Glycin, or ascorbic acid.[266]

ASSOCIATED DEVELOPER SALTS

Developing agents that contain only —OH groups are acidic and need alkali in the developing solution to become active. Such developing agents are reasonably stable in air and are sold as the free developing agent. Hydroquinone is an example. Developing agents containing one or more $-NH_2$ are basic in character and will react without the need of alkali in the developing solution, although sometimes very slowly. Such amino developing agents are unstable in air. The free base, *N*-methyl-*p*-aminophenol, for example, deteriorates quite rapidly. The free bases of developing agents, that is, those containing $-NH_2$ groups, are reacted with acids to form salts that are more stable in air than the free-base developing agent alone. Thus, *N*-methyl-*p*-aminophenol is sold as the sulfate salt (Metol).

Almost any amino developing agent may be reacted with an acid to produce a developer salt. The acidic portion of the salt must be neutralized later with an alkali to make the developing agent active. A. and L. Lumière and A. Seyewetz[267–269] reacted sulfur dioxide or sulfurous acid with the free bases of *p*-aminophenol, *N*-methyl-*p*-aminophenol, and *p*-phenylenediamine. The white crystalline compounds were stable in the solid state, producing sodium sulfite and the active developing agent in alkaline solution. *N*-Methyl-*p*-aminophenol combines with sulfurous acid to produce a compound that is active when dissolved in only sodium sulfite solution. Sulfurous acid has been combined with developing agents that are to be coated in emulsion layers.[270]

Most free-base developing agents are sold as salts of hydrochloric, hydrobromic, oxalic, sulfuric, or *p*-toluene sulfonic acids. Salts of 2,4-diaminophenol, *N*-methyl-*p*-aminophenol, and *p*-phenylenediamines with naphthalene-1,5-disulfonic acid, diphenyl-4,4′-disulfonic acid, or *p*-sulfobenzoic acid have been patented.[271] Salts generally dissolve more rapidly than the free-base compound. Phenidone is slow to dissolve, and it would be expected that salt formation of this developing agent would aid its solubility. In practice, the sulfate and hydrochloride salts of Phenidone are of little value, as the 1-phenyl-3-pyrazolidone is deposited as soon as the salt dissolves in water. The toluene, xylene, naphthalene, and anthracene mono- and polysulfonic acid salts of Phenidone and its derivatives are claimed to dissolve rapidly without deposition of the free developing agent. According to British Patent 943,928,[272] "It is believed that the salts probably decompose when added to the aqueous solution of pH above 7 and the freed aromatic sulphonic acid acts as a medium assisting the dissolution of the freed base."

A free-base developing agent and an acidic developing agent may be combined to form an associated developer salt. In solution, two developing

agents would be released, often forming superadditive developing combinations. Some associated developer salts develop without the addition of alkali to the solution. The combinations of acidic developing agents with free-base developing agents were investigated in 1899 by A. and L. Lumière and A. Seyewetz.[273] Hydroquinone or catechol was found to associate with *p*-phenylenediamine or *o*-phenylenediamine. These investigators prepared the combination of pyrogallol and *p*-phenylenediamine and other associated developer salts. The combination of hydroquinone and *p*-phenylenediamine was in 1:1 molecular proportion.[274] The combination of *p*-phenylenediamine with catechol, pyrogallol, or chlorohydroquinone was patented in 1937 by Frank Clement Starnes as a fine-grain developer in sodium sulfite solution.[275] Catechol and *o*-phenylene diamine formed a 1 : 1 compound which produced a rapid developer.[276]

An outstanding example of an associated developer salt was the combination of hydroquinone with *N*-methyl-*p*-aminophenol. This combination was patented by Lumière[277] in 1902 and sold as Metoquinone. Metoquinone was a salt composed of one molecule of hydroquinone associated with two molecules of *N*-methyl-*p*-aminophenol.[278,279] A. and L. Lumière[280] devised a number of formulas for plate and paper developers using Metoquinone, but the fact that it cost more than Metol-hydroquinone developers limited the use of the associated developer salt.

Robert C. Lyon[281] prepared associated developer salts containing three developing agents in combination to make fine-grain developing solutions capable of providing high-speed images. Crystalline ternary addition compounds included:

1. Catechol:*p*-aminophenol:*p*-chloro-*o*-phenylenediamine in 1:1:1 proportions.
2. Hydroquinone:*o*-aminophenol:*o*-phenylenediamine in 2:1:4 molecular proportions.
3. Chlorohydroquinone:*p*-aminophenol:*o*-phenylenediamine in 1:1:2 molecular proportions.

In 1958 G. I. P. Levenson and M. G. Rumens[282] analyzed the large, needle-shaped crystals that were deposited from a concentrated liquid developer containing Phenidone and hydroquinone. The various analyses indicated that the crystals consisted of 40% hydroquinone and 60% Phenidone—that is, an addition compound consisting of one molecule of hydroquinone with one molecule of Phenidone. This compound was called "Phenoquinone" by analogy with "Metoquinone," the addition compound of Metol base and hydroquinone. Later, the precipitate from a concentrated Phenidone-hydroquinone developer was analyzed by E. Mutter and W. Schneider.[283]

An equimolar complex of Phenidone and hydroquinone was found to have been formed. In studying this molecular addition compound, K. Kurosaki[284] found that the compound "is formed by hydrogen bonding between C=O of 1-phenyl-3-pyrazolidone and OH of hydroquinone in the form of $\diagdown C{=}O\cdots H{-}O{-}$. This hydrogen bond would become weak in an aqueous solution; but, even in this case, oxidation of 1-phenyl-3-pyrazolidone is suppressed by the protection of the peptide linkage by hydroquinone."

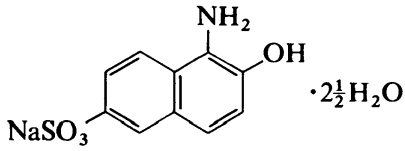
Some of the more important associated developer salts that were commercially important in the past are:

Metoquinone	A combination of two molecules of Metol base with one molecule of hydroquinone.
Chloranol	A combination of two molecules of Metol base with one molecule of chlorohydroquinone.
Hydramine	A combination of one molecule of para-phenylenediamine with one molecule of hydroquinone.[285]
Pyramidol	A combination of one molecule of para-aminophenol base with one molecule of hydroquinone.
Meritol	A combination of one molecule of catechol with one molecule of para-phenylenediamine base, still used today in the fine-grain developer Meritol.
Ortol	An apparent mixture of two molecules of the sulfate salt of ortho-aminophenol with one molecule of hydroquinone.[286,287]

Although associated developer salts are neutral, they are capable of developing latent images without the need for alkali in the developing solution.

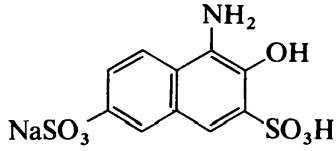
OTHER PREVIOUSLY USED PRACTICAL DEVELOPING AGENTS

Fallen into disuse are two similar organic developing agents:[288]



Eikonogen

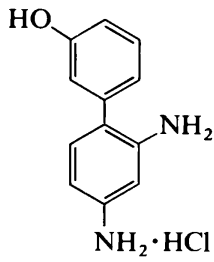
(1-amino-2-naphthol-6-sulfonic acid, sodium salt)



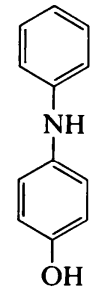
Diogen

(1-amino-2-naphthol-3-sulfo-6-sodium sulfonate)

Other commercial developing agents, not currently in use, include:

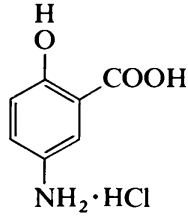


Diphenal



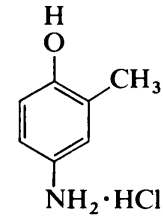
Duratol

(para-hydroxydiphenylamine)



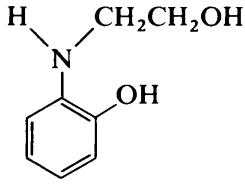
Neol

(hydrochloride salt of para-aminosalicylic acid)



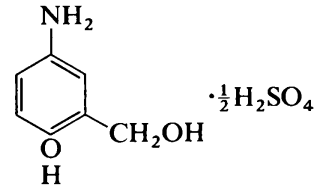
Monomet

(2-methyl-4-aminophenol hydrochloride)



Atomal

N-(hydroxyethyl)-*o*-aminophenol



Edinol

3-(hydroxymethyl)-4-hydroxy aniline sulfate

METAL-ION DEVELOPERS

Iron

Ferrous ions (Fe^{2+}) are capable of acting as developing agents for exposed silver halide, but the rate of development is extremely slow.[289] Ferrous sulfate, according to M. Carey Lea,[290] has little effect on the latent image

unless a soluble silver salt is present in the developing solution. In 1877 Carey Lea found that "In the presence of many organic acids, iron acquires the property of attacking and reducing the latent image in the absence of a soluble silver salt, and so producing a visible image." Ferrous lactate, salicylate, or succinate formed vigorous developing solutions, but ferrous oxalate was the most active of all the ferrous salts tried. Later Carey Lea[291–293] proposed to add borax, sodium sulfite, or sodium phosphate to potassium oxalate–ferrous sulfate solutions. Ferrous oxalate, however, was widely used for early dry plate and film materials. The method of development by ferrous oxalate was extensively investigated by S. E. Sheppard and C. E. Kenneth Mees.[294,295] Development was found to take place as shown in the following reaction:[296]

$$\underset{\text{silver ion}}{Ag^+} + \underset{\text{ferrous oxalate}}{Fe(C_2O_4)_2^{2-}} \rightleftharpoons \underset{\text{metallic silver}}{Ag} + \underset{\text{ferric oxalate}}{Fe(C_2O_4)_2^-}$$

In the presence of excess oxalate in the developing solution, the ferric oxalate ion becomes $Fe(C_2O_4)_3^{3-}$. It has been suggested that $Fe(OH)_2$, or the $FeOH^+$ ion, is the active developing agent.[297]

An even more active developer than ferrous oxalate is formed when ferrous ions are complexed by ethylenediamine tetraacetic acid (EDTA).[298,299] T. H. James[300] found that the active agent in development was the ferro-EDTA complex rather than the ferrous ion. Ferro-EDTA solutions of high concentration showed relatively little change of activity in either moderately acid or alkaline solutions. Silver halide solvents, such as potassium thiocyanate or thiourea,[301] accelerated the rate of development.

Titanium

Titanium trichloride dissolved in aqueous potassium oxalate produces an active developing solution. J. Rzymkowski[302–305] investigated this developer around 1940, but the developing action of titanium appears to have been known as early as 1905.[306] The simple reaction involved:

$$\underset{\text{Titanous ion}}{Ti^{3+}} + \underset{\text{silver ion}}{Ag^+} \rightleftharpoons \underset{\text{metallic silver}}{Ag} + \underset{\text{titanic ion}}{Ti^{4+}}$$

In practice, this reaction ceases almost as soon as it starts, because the titanic ion attacks the metallic silver to produce silver ions. The reaction can be made to form a metallic silver photographic image if an acceptor is present to tie up the oxidized form of the metal ion. As with the iron developer, potassium

Table 1. Properties of the Major Developing Agents

Common Name	Hydroquinone	Chloro-hydroquinone	Catechol	Pyrogallol	para-Aminophenol	Amidol
Scientific names	1,4-Dihydroxy-benzene; para-dihydroxy-benzene	2-Chloro-1,4-di-hydroxybenzene; 2-chloro-1,4-benzenediol	1,2-Dihydroxy-benzene; ortho-dihydroxy-benzene	Pyrogallic acid; 1,2,3-trihydroxy-benzene; 1,2,3-benzene triol	4-Amino-1-hydroxy-benzene hydrochloride; para-hydroxyaniline hydrochloride	2,4-Diaminophenol dihydrochloride
Commercial names	Quinol, Tecquinol, Hydroquinol	Adurol, Chloroquinol	Pyrocatechin	Piral Pyro	Activol, Azol Kodelon, Para, Rhodinal	Acrol, Dianol
Form	Needle-shaped crystals	Needles or leaflets	Needles from water	White crystals	Free base: plates from water. Hydrochloride salt: crystalline.	Crystals
Molecular weight	110.11	144.56	110.11	126.11	Free base: 109.12. Hydrochloride salt: 145.5.	197.01
Melting point (°C)	170	103	105	131–133	Free base: 190. Hydrochloride salt: decomposes about 306.	205

Solubility in water (g in 100 ml at 20°C)	8	92	30	40	Free base: 1.2. Hydrochloride salt: 10.	25
Solubility in solvents	Soluble in alcohol and ether. Slightly soluble in benzene.	Soluble in alcohol. Slightly soluble in ether and chloroform.	Soluble in alcohol, benzene, chloroform, ether, pyridine.	Soluble in alcohol and ether. Slightly soluble in benzene and chloroform.	Free base soluble in alcohol and ethyl methyl ketone, slightly soluble in ether, almost insoluble in benzene and chloroform. Hydrochloride salt is soluble in alcohol and slightly soluble in ether.	Free base is slightly soluble in alcohol and acetone, very slightly soluble in ether and chloroform. Hydrochloride salt is soluble in alcohol.
Human toxicity	Relatively safe in very low concentrations. Ingestion of 1 g or more may cause serious complications. Contact with skin may cause dermatitis.		Can cause eczematous dermatitis. Ingestion can cause very serious complications. Avoid contact with large areas of skin.	Severe poisoning may result from percutaneous absorption. Inhalation can cause asthma.	Can cause dermatitis and skin sensitization. Inhalation can cause asthma.	Pure compound or oxidation products may cause eczematoid contact dermatitis or bronchial asthma.

Table 1. (*continued*)

Common Name	Metol	Glycin	para-Phenylene-diamine	L-Ascorbic Acid	Phenidone
Scientific names	Monomethyl-para-aminophenol sulfate; para-methylamino-phenol sulfate	para-(Hydroxy-phenyl) glycine; para-hydroxy-phenylamino-acetic acid	para-Diaminobenzene; 1,4-diaminobenzene	L-Xyloascorbic acid; hexuronic acid	1-Phenyl-3-pyrazolidone; 1-phenyl-3-pyrazolidinone
Commercial names	Elon, Genol, Graphol, Pictol, Photol, Rhodol	Athenon, Glycin, Monazol, Inconyl	Free base: Diamine, Paramine, Metacarbol. Hydrochloride salt: Diamine H, P.D.H., p.p.d.	Vitamin C, many pharmaceutical names such as Ascorin, Cevitex, Cevimin	Phenidone, Graphidone
Form	Crystals	Leaflets from water	White crystals	Crystals (plates or needles)	Leaflets or needles from benzene

Molecular weight	344.38	167.16	108.14	176.12	162.19
Melting point (°C)	Free base: 87 Sulfate salt: 260 with decomposition	Browns at 200, begins to melt at 220, completely melted at 247 with decomposition	Free base: 145–147. Hydrochloride salt: Decomposes without melting.	190–192 some decomposition	121
Solubility in water (g in 100 ml at 20°C)	4	0.02	1	30	2
Solubility in solvents	Free base very soluble in alcohol, ether, and hot water. Sulfate salt slightly soluble in alcohol and ether, insoluble in benzene.	Low solubility in alcohol, acetone, ether, and benzene	Free base soluble in alcohol, chloroform, ether. Hydrochloride salt soluble slightly in alcohol and ether.	Soluble in alcohol and propylene glycol,. Insoluble in ether, chloroform, benzene.	Soluble in alcohol and benzene. Almost insoluble in ether.
Human toxicity	Can cause skin irritation or sensitization.		Pure compound or oxidation products may cause eczematoid contact dermatitis or bronchial asthma.	Essential vitamin in human nutrition	Low oral toxicity. No reported cases of dermatitis.

oxalate may be used for this purpose, but mono-, di-, and tricarboxylic acids, such as acetic, malonic, or citric acids, form developers with metal ions such as iron or titanium.

The combination of a metal ion such as titanium and a modern chelating agent produces a solution of high photographic activity. Although several chelating agents have been used successfully, ethylenediamine tetraacetic acid and its sodium salts have generally been preferred in making titanium developers. Ti^{3+}-EDTA developers are highly acid but can be regenerated electrolytically or chemically.[307,308] G. M. Haist et al.[309] found that although regeneration of the developer was possible, combined titanium-EDTA-mercaptosuccinic acid solutions (monobaths) were less capable of regeneration because of stain formation. The complexes of Ti^{3+} and Fe^{2+} with EDTA and similar chelating compounds have been used by T. H. James and W. Vanselow[310] and H. J. Price[311] to study the mechanism of development.

Vanadium

The developing properties of vanadium salts were studied as early as 1894 by Auguste and Louis Lumière.[312] Highly acidic vanadium developers may be electrolytically regenerated, according to Pierre Roman,[313] who found that vanadium bromide developer produced in 15 to 20 sec at ambient temperature an image comparable with a 5- to 10-min development in a conventional developer. Development of motion picture film with continuous regeneration of the vanadium developer was extensively studied by A. A. Rasch and J. I. Crabtree.[314,315]

Copper

In 1878 M. Carey Lea[316] treated ammoniacal cupric oxalate with zinc filings to produce cuprous oxalate. When ammoniacal cuprous oxalate was added to water, the solution, according to Carey Lea, "exhibited considerable power as a developer." Auguste and Louis Lumière[317] studied the developing properties of ammoniacal cuprous chloride in 1887. Johannes Rzymkowski,[318] besides studying the iron and titanium developers, also investigated cuprous ammonium (or amine) tartrate or citrate developing solutions.

Other Metal Ions

Development by chromous ion was first mentioned by R. E. Liesegang[319] in 1895 and later by E. Fuchs.[320] Recently, the mechanism was thoroughly studied by Harry J. Price.[321] Price has also reported that $Ru(NH_3)_6^{2+}$ was a

selective developer. Tungsten, molybdenum, and cobalt have also been reported to act as developing agents for silver halide materials.[319,322]

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Chapter 5
The Function of Developer Constituents

Development is a fairly complex heterogeneous reaction, the mechanism of which is not yet completely understood.

K. S. LYALIKOV[233]

THE DEVELOPING AGENT

The developing agent supplies the electrons to amplify the latent image; it may, however, give its electrons to other than the latent image. Oxygen from the air, dissolved in the developing solution, is seeking to gain electrons. Certain sites on the surface of unexposed silver halide crystals in the emulsion layer also will accept electrons from the developing agent. Compounds are needed in the developer to activate, to protect, and to guide the developing agent so that the maximum amplification of the latent image is obtained. Of the many developing agents available, some may act alone, but most practical developing solutions require chemical teamwork of two developing agents for optimum results.

Developing solutions, usually called developers, are water solutions of the developing agent that also contain

- A preservative to protect and sustain the developing agent against the undesirable loss of electrons.

- An alkali to activate the developing agent to secure the desired ease of electron release.
- A restrainer to restrict the developing agent's donation of electrons only to the exposed silver halide crystals.

Developers usually contain a separate compound to accomplish each of these helping actions for the developing agent. Certain developing agents are energetic enough to transfer electrons without the presence of an alkali in the solution, but most practical developers require an alkaline environment, particularly if the action is to be rapid. Energetic developing solutions often require a restrainer or antifoggant compound to inhibit the reduction of unexposed silver halide crystals. A preservative is needed to maintain the developing action without serious loss during the life of the developer and to prevent staining from the used developing agent. Practical developers may also contain additional compounds to accomplish specific purposes, such as preventing the precipitation of salts from hard water used to prepare the solution.

THE PRESERVATIVE

Sodium Sulfite

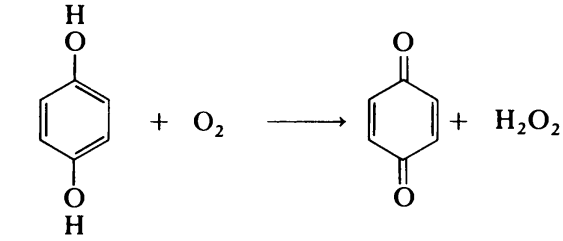
The universally used preservative in negative developers is sodium sulfite. This compound was first proposed by H. B. Berkeley[1,2] in 1882 to prevent the staining of negatives by the oxidation products of a pyrogallol developer. Ever since 1882 most developing solutions have contained some sulfite ions, but the universal use of this compound is the result of more than just its protective action. At first the action of sulfite was little understood, but studies through the years have revealed much about this compound.[3–19] Some of its multifold action in developing solutions may be classified under the following headings:

Antioxidant Action

Sulfite solutions are known to be readily oxidized in the air,[20,21] although sodium sulfite–potassium metabisulfite solutions have better keeping properties.[22] Oxygen of the air is absorbed into water solutions of developing agents. This oxygen may rob the developing agent of its electrons, converting the developing agent into its oxidized form—a form useless for developing action. Sodium sulfite in the developer can react with the absorbed oxygen,

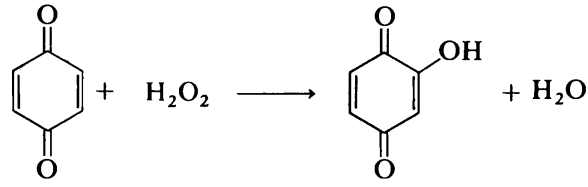
producing harmless sodium sulfate, but preserving the strength of the developing agent.

Absorbed oxygen in an alkaline solution of the developing agent, such as one containing hydroquinone, may react as follows:



hydroquinone oxygen quinone hydrogen peroxide

Hydrogen peroxide, according to T. H. James, J. M. Snell, and A. Weissberger,[23] may then react with the quinone, forming hydroxyquinone and water.



quinone hydrogen peroxide hydroxyquinone water

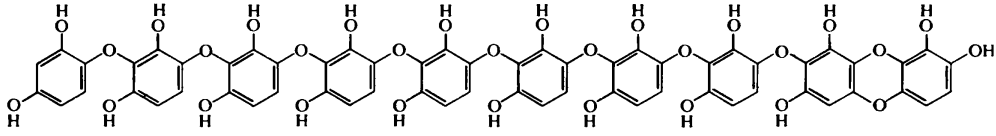
Hydroxyquinone may interact with itself, forming dark brown products of low solubility that stain the gelatin. Quinone itself is capable of a number of color-forming reactions.[24] In the presence of sodium sulfite, however, most of the color-forming reactions do not occur, and insoluble products are not formed. The sulfite ion removes any hydrogen peroxide, blocking the formation of the hydroxyquinone.

$$\underset{\text{hydrogen peroxide}}{H_2O_2} + \underset{\text{sodium sulfite}}{Na_2SO_3} \longrightarrow \underset{\text{sodium sulfate}}{Na_2SO_4} + \underset{\text{water}}{H_2O}$$

Chain-Breaking Action

Once started, the oxidation of a developing agent, such as hydroquinone, tends to accelerate because of the presence of the oxidized forms.[25] When hydroquinone loses one electron, it forms a semiquinone; when it loses two, quinone is formed. These oxidized forms may then react with hydroquinone itself. For example, one molecule of quinone may react with one molecule of

hydroquinone to form two molecules of the semiquinone—a highly reactive but unstable form of hydroquinone that is deficient one electron. Or two quinone molecules may react with themselves, yielding one molecule of hydroxyquinone and one molecule of hydroquinone. As already indicated, hydroxyquinone may react with itself to produce insoluble brown products, usually referred to as humic acids (similar to the humic acids produced from humus in the soil).[26,27] The structure of a humic acid, as given by Heinrich Thiele and Helmut Kettner,[28] required 10 hydroxyquinone molecules for its formation:



Although the above description of the possible interaction of the oxidized forms of a developing agent may sound complicated, in fact only a few of the possible reaction mechanisms have been mentioned.

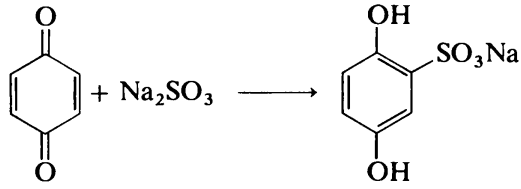
The oxidation of hydroquinone proceeds in two steps: a slow step involving the loss of one electron to form the half-oxidized form of hydroquinone known as semiquinone, and a second, more rapid loss of another electron to change the semiquinone into the quinone. When quinone reacts with hydroquinone, forming two semiquinone molecules, the slow step in the oxidation of hydroquinone is by-passed. Hydroquinone, therefore, is much more unstable in the presence of the quinone. By removing the oxidation products of hydroquinone, probably at the semiquinone stage, sodium sulfite breaks the catalytic chain reaction that would degrade so rapidly an unprotected developing solution.

This chain-breaking action of sodium sulfite, rather than the reaction between sulfite and the oxygen from the air, is the primary protective action involved in preserving a developing solution. Reactions between sulfite and the oxidized forms of most of the other developing agents occur in a similar manner, but pyrogallol may still form some insoluble, colored oxidation products in the image areas of a negative, even though some sodium sulfite is present. The sodium sulfite cannot react with these colored but highly insoluble staining products. Sodium sulfite does not appear to react with the oxidized forms of 1-phenyl-3-pyrazolidone or L-ascorbic acid as the sulfite does with benzene type of developing agents.

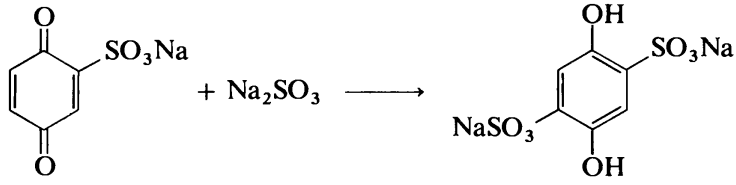
Solution Decolorizing Action

The oxidized developing agent in the presence of sulfite is capable of developing activity.[29] When sodium sulfite reacts with the oxidized forms of a de-

veloping agent, the sulfite adds to the oxidized molecule to form a new compound. Quinone reacts with sodium sulfite to yield sodium hydroquinone monosulfonate.

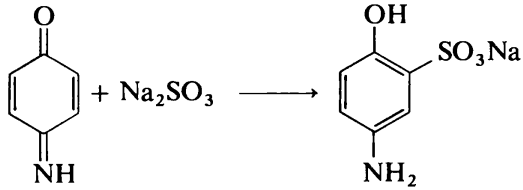


Sodium hydroquinone monosulfonate is a weak developing agent whose oxidized form (quinone monosulfonate) may also react with sulfite.



The disulfonate of hydroquinone is not very reactive, and further sulfonation usually does not occur.

The oxidized forms of other developing agents may react in a similar manner to quinone. Quinoneimine is the oxidized form of *p*-aminophenol. Quinoneimine reacts with sodium sulfite to form sodium-*p*-aminophenol monosulfonate.



The disulfonate may be formed as with quinone. Developing agents that are not derivatives of benzene, such as L-ascorbic acid, do not form sulfonates.

The mono- and disulfonates formed by the reaction between the oxidation products of many developing agents and sodium sulfite are colorless, water-soluble compounds. The formation of the dark staining products of the oxidation of developing agents is prevented. And the monosulfonate formed still possesses some activity as a developing agent.[30]

Maintenance of Developer Activity

The presence of the oxidized forms of the developing agent may enhance or inhibit the development of the latent image.[31] Compounds containing only

hydroxy groups have oxidation products that accelerate the developing action in many cases. *p*-Hydroxyphenylglycine acts as though it were a member of this class of compounds. Developing agents containing amino or substituted amino groups have oxidation products that restrain the activity, particularly in solutions of low alkalinity. A few developing agents have oxidation products that do not seem to influence the rate of development.

By forming sulfonates with many of the oxidized forms of the developing agents, sodium sulfite decreases the concentration of the oxidized form to such a low value that the initial rate of development is not materially influenced by the oxidized forms. Sodium sulfite thus acts to stabilize and maintain a uniform developing action by the developing agent. The effect of sodium sulfite upon the oxidized forms of various developing agents is listed in Table 1, derived mainly from the work of T. H. James.[32]

The action of the oxidized forms of developing agents may be utilized to form special-purpose developers. Hydroquinone, catechol, and pyrogallol have oxidation products that accelerate development. Developers in which such oxidation products are allowed to accumulate can produce unusually high-density, high-contrast images on suitable silver halide emulsions. Images

Table 1. Effect of Sodium Sulfite on the Oxidized Forms of Developing Agents

Developing Agent	Effect of Oxidized Form on Rate of Development	Effect of Sulfite on Rate of Development
Hydroquinone	Increase	Decrease
Catechol	Increase	Decrease
Pyrogallol	Increase	Decrease
p-Hydroxyphenylglycine	Increase	Decrease
Elon monosulfonic acid	Increase	Decrease
p-Aminophenol	Decrease	Increase
Elon	Decrease	Increase
p-Aminophenylglycine	Decrease	Increase
p-Aminodimethylaniline	Decrease	Increase
sym-Dimethyl-*p*-phenylenediamine	Decrease	Increase
p-Aminodiethylaniline	Decrease	Increase
Phenidone	Decrease	None
L-Ascorbic acid	None	None
Hydroxylamine	None	None
Potassium ferroöxalate	None	None

produced in the presence of such oxidation products are also tanned; that is, the gelatin in the image area has reacted with the oxidation products to form a gelatin layer that is less water-soluble than before. If a photographic film with an unhardened gelatin layer is used, the soft nonimage area after development may be dissolved away with warm water, leaving a relief gelatin image that is suitable as a matrix for making dye-transfer color prints. Developers utilizing oxidation products can contain only a very little sulfite ion, making such developers unstable and suitable only for one-time usage. Color photographic processes are dependent upon the reaction of an oxidized developing agent with a color-forming substance.[33] The amount of sulfite ion in these developers controls the extent of action by the oxidation products. (See Figure 1.)

Silver Solvent Action

Sulfite ions in the developer may combine with the silver ions from the silver halide grains to produce a soluble complex ion, $Ag(SO_3)_2^{3-}$.[34] Silver chloride is considerably more soluble than silver bromide. But high concentration of sodium sulfite can dissolve silver bromide grains in the times normally required for development.[35,36] Only a few silver ions from the chloride or bromide grains are capable of existing in only a water solution. No other ions may then dissolve from the grains. Sulfite ions remove the few silver ions from the developer solution by forming the complex silver sulfite ions; then, an equal number of silver ions from the grains may go into solution to replace them. The rate at which the silver ions dissolve, as well as the number, is increased by the presence of sulfite ions in a developer.

The complex ion of silver and sulfite is not a stable union under the alkaline conditions of a developer. This complex ion then yields the original ions.

$$Ag(SO_3)_2^{3-} \rightleftharpoons Ag^+ + 2SO_3^{2-}$$

As soon as the silver ions are released in a developer, they will be reduced to metallic silver, usually upon the metallic silver filaments of the image being formed by chemical development. Fine-grain images may result from this solution physical development. Several practical commercial developers utilize high-sulfite concentrations to promote fine-grain development. A combined developer-and-fixer has been patented that contained only Metol and a high concentration of sodium sulfite.[37]

Developers containing high concentrations of sodium sulfite may produce fine-grain images by another result of solvent action. The silver halide grain is pitted and etched by the removal of the silver ions by the sulfite.[38] The physical size of the grain is diminished. The distance between nearby grains may be increased. Grains that touch may be separated from contact. When

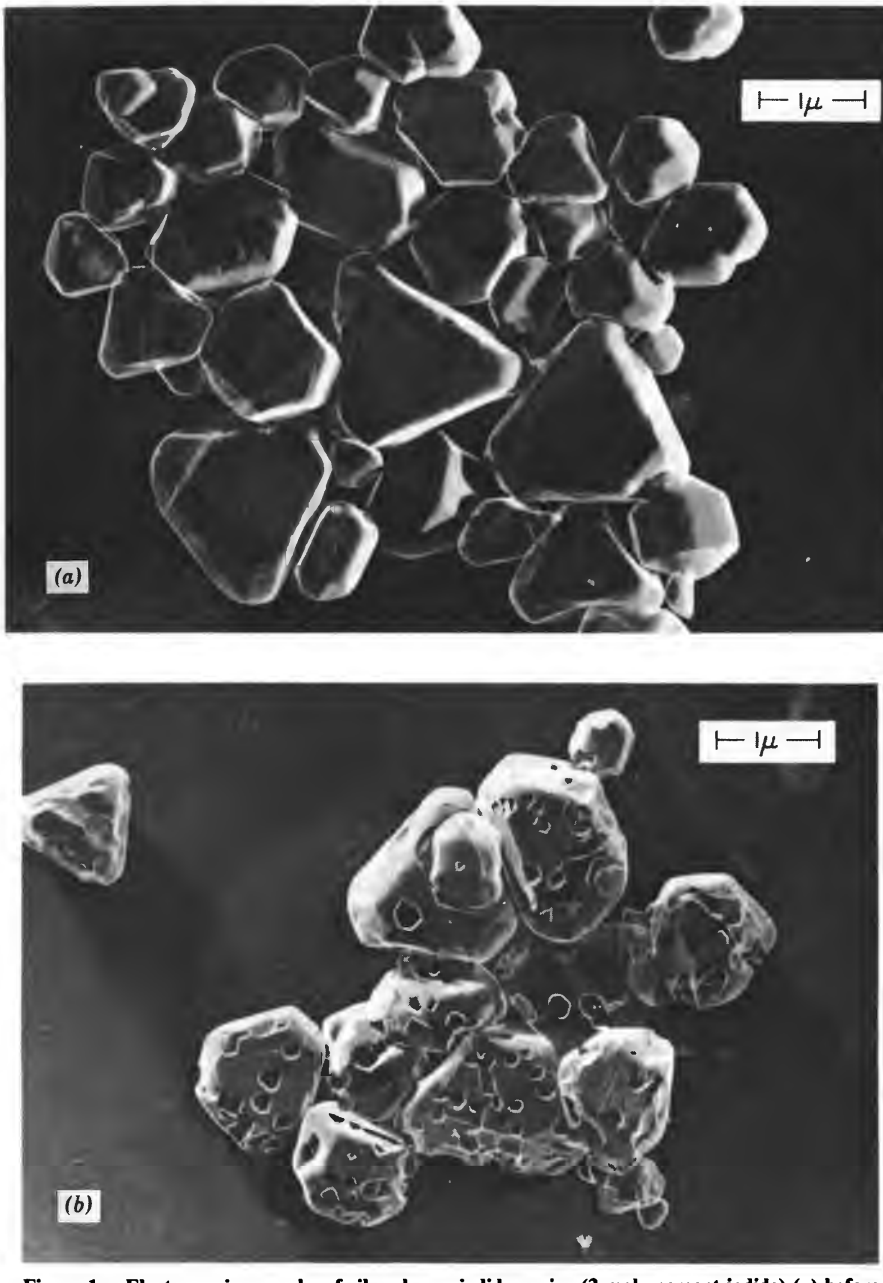


Figure 1. Electron micrographs of silver bromoiodide grains (3 mole percent iodide) (*a*) before and (*b*) after etching for 1 min in 1% sodium sulfite. [J. F. Hamilton, L. E. Brady, and F. A. Hamm, *J. App. Phys.*, 29: 801 (1958)]

the distance between the silver halide grains is increased, the distance between the masses of silver filaments produced by development will also be increased, resulting in a more even distribution in the developed image. This image will appear to the eye to be less grainy, because the solvent action of the sulfite has reduced the clumping of the grains before complete development had occurred.

Other silver halide solvents have been reported to have beneficial results when used in sulfite-containing developing solutions. In 1896 J. M. Eder[39] found that sodium thiosulfate in a Metol-sodium sulfite-sodium carbonate developer produced "greater detail." Small quantities of potassium thiocyanate (0.003 g/liter or 0.02 to 1%) were patented in sulfite-containing developers to accelerate the speed of development without increasing granularity.[40] T. H. James and W. Vanselow[41] found that "The combination of 1.0 g of potassium thiocyanate with sodium sulfite is definitely more effective in promoting the rate of solution of silver halide than would be expected on the basis of simple addition of the rates of solution in each solvent by itself." These two investigators determined the amount of various silver halide solvents necessary to increase the rate of solution in a Metol–*d*-araboascorbic acid developer to 1.7% per minute (20.8°C). These quantities are given in Table 2.

The solvent action of sodium sulfite or other compounds may have some undesirable effects. The physical developing action of the silver sulfite complex ion may result in increased fog. The silver sulfite complex is still present

Table 2. Amount of Silver Halide Solvent to Produce Equal Rate of Solution

	Concentration	
Agent	g/liter	part of molecular weight
Potassium thiocyanate	0.5	0.005
2-Aminomethyl thiophene	2.66	0.023
Ethylenediamine	1.5	0.025
2-Aminomethyl furane	2.8	0.028
n-Butylamine	2.9	0.04
Isopropylamine	2.75	0.046
Hydroxylamine sulfate	26.2	0.16
Potassium chloride	16.5	0.22
Triethylamine	34.0	0.34

in the used developer after the solution is returned to the bottle for storage. The complex is a weak one, and the silver ion is slowly released from the sulfite ion. The silver ion is reduced to metallic silver in the solution and then falls to the bottom of the bottle as a dark sludge. This dark precipitate is often seen in developers containing a high concentration of sodium sulfite.

The silver complex may be reduced during the developing period and deposited upon the surface of the photographic material, forming a silver stain or scum. The silver stain is more likely to be formed with used developing solutions or upon aged silver halide negative photographic films. The stain will be given with developers containing a considerable quantity of sodium sulfite but also those with silver halide solvents such as ammonium chloride, ammonium thiocyanate, diethanolamine, ethanolamine, ethylenediamine, sodium or ammonium chloride, sodium or potassium thiocyanate, sodium or ammonium thiosulfate, or other similar compounds. The staining in solvent developers or combined developers-and-fixers is said to be prevented by adding to the developing solution 0.2 g and upwards of chlororesorcinol[42] or about the same quantity of 2,4-dihydroxybenzophenone.[43]

Increasing of Emulsion Speed

The solvent action of sodium sulfite also has other effects. By etching away some of the surface of the silver chloride or silver bromide grains, sulfite ions make available for development latent image sites that were buried beneath the surface of the grain.[44,45] This mild solvent action by the sulfite ions is especially effective in increasing the relative rate of development of silver halide grains that had received low exposure.[46] Gerald I. P. Levenson[47] found "the speed on negative film was reduced $3\frac{1}{2}$ times on reducing the sulphite concentration to one quarter." This increase in developability in the shadow areas of the negative may produce a significant increase in the emulsion speed of the photographic material. By uncovering subsurface latent image sites and by decreasing the time it takes to begin the development of very small latent image centers, sulfite ions give considerable increases in the amount of silver produced.

The reinforcement of very small latent image centers by the physical developing action of sulfite may also be important in increasing their rate of development, particularly in developer solutions of lower alkalinity.[48] Physical development of silver dissolved from an unexposed grain upon the latent image of a developing grain promotes the solution of the unexposed grains. Thus, silver from unexposed grains is made to contribute to the final silver contained in the developed image from an exposed grain.

The increase in emulsion speed given by sodium sulfite is especially pronounced with developing agents that act as doubly charged ions, such as hydroquinone, but less with singly charged developing agents.[49] The formation of the silver sulfite complex ions on the surface of the grain may disrupt the normal state of the surface. This disruption may make it easier for a highly charged developing ion to approach the grain surface to initiate development by electron transfer. Small quantities of silver halide solvents, such as sodium thiosulfate or potassium thiocyanate or organic amines, in developers have also been observed to give increases in emulsion speed.

Normal development times are relatively short for sulfite ions to act upon the difficult-to-dissolve silver bromide grains contained in the higher-speed photographic materials. A series of photomicrographs has shown[38] that sodium sulfite, at 125 g of sulfite per liter of developing solution, is quite capable of dissolving silver bromide grains completely during the time normally required for development of the latent image. The solution physical developing action of sulfite ions materially enhances the emulsion speed of silver halide materials processed in sulfite-containing developers.

Other Effects of Sodium Sulfite

Sodium sulfite in the developing solution has all the described actions—and more. High concentrations of neutral and alkaline salts are known to provide considerable protection against aeration because the presence of the salt in solution reduces the solubility of the oxygen in the solution.[50] Usually, high concentrations of sodium sulfite are present in the developer, providing additional inhibition of aerial oxidation by its salt effect. Sodium sulfite is also a weak alkali. In some developers this amount of alkali is sufficient to make active developers with only the developing agent and sulfite present. The presence of the sulfite ions, especially at the higher concentrations, may also influence the color of the silver image. All these listed actions of sodium sulfite, plus probably some still unrecognized as yet, have made sodium sulfite almost the universal "preservative" to be found in developers.

Other Sulfite Salts

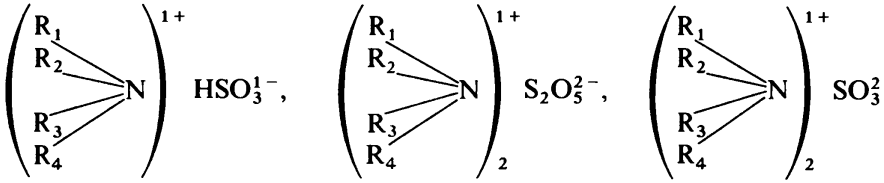
Sodium sulfite is available in anhydrous form, often called desiccated, or in a crystal form that contains seven molecules of water of crystallization. The crystal form requires twice the weight of the anhydrous form.[51] Other sulfite salts are used for developers for special purposes. Potassium sulfite is chosen for concentrated liquid developers because of the higher solubility of the potassium salt. A liter of water was reported by K. Frank[52] to dissolve 1070 g of potassium sulfite compared to 266 g of sodium sulfite. As early as

1888, only six years after Berkeley proposed the use of sodium sulfite, the commerical firm of Mawson and Swan suggested potassium metabisulfite as a replacement.[53,54] Potassium bisulfite was used by William Brooks[55] a year before that, and ammonium bisulfite was suggested four years later.[56]

Sodium or potassium metabisulfite, $Na_2S_2O_5$ or $K_2S_2O_5$, can replace sodium sulfite because these compounds are converted to sulfite ions in alkaline solution.[57] One hundred grams of sodium sulfite may be replaced by only 44 g of potassium metabisulfite. Because of the acid character of the metabisulfite, however, for each 10 g of metabisulfite used 3.6 g of sodium hydroxide or 9.5 g of anhydrous sodium carbonate will be needed to maintain the same solution alkalinity.[58] The metabisulfites in solution yield the acidic bisulfite ion, HSO_3^-. When neutralized with an alkali, the sulfite ion, SO_3^{2-}, is formed. The less expensive, more available, and more soluble sodium bisulfite, $NaHSO_3$, may be used to replace the potassium metabisulfite. Both compounds yield the bisulfite ion, HSO_3^-, in solution. R. W. Henn and J. I. Crabtree[59] found that 84 g of the sodium bisulfite was, for most purposes, the photographic equivalent of 100 g of the potassium metabisulfite.

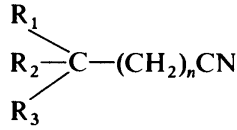
Developers for high contrast or gelatin-tanning require that the free sulfite ion be present only in low concentration. Acetone bisulfite or formaldehyde bisulfite compounds are used in place of sodium sulfite because these carbonyl bisulfite compounds have most of the sulfite ion in an unavailable form. Only a small amount of the sulfite is freed as the ions are used. Cyclohexanone sodium bisulfite has been claimed to have superior characteristics for use as the sulfite buffer.[60] Aeration life of the developing solution was claimed[61] to be improved when sodium formaldehyde bisulfite was combined with the sodium or potassium bisulfite compounds of acetone, acetaldehyde, aldol, isobutyraldehyde, methyl ethyl ketone, glyoxal, or methoxyacetaldehyde. The addition of 1,2-diamines, such as 1,2-ethylenediamine or 1,2-propylenediamine, has been patented[62] for use in sodium sulfite solutions to improve the resistance to aerial oxidation.

Quaternary ammonium bisulfites, pyrosulfites, and sulfites[63,64]



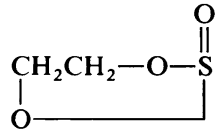
(where R_1, R_2, R_3, and R_4 are carbon chains of from one to four atoms or hydroxy-substituted chains of two to four carbons) are said to form developer concentrates of lower viscosity than hydroxyalkylamine-sulfur dioxide addition products that have been used for this purpose. From about

10 to 20 g of a compound such as tetramethyl ammonium bisulfite (55% solution) was used as the sole source of sulfite ions in photographic developers. Polyquaternary ammonium bisulfites, pyrosulfites, and sulfites have also been patented as developer preservatives.[65] Compounds having the general formula

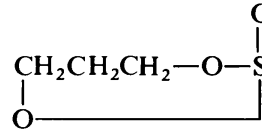


(where R_1, R_2 and R_3 are hydrogen atoms or unsubstituted carbons chains with not more than four carbon atoms and n is 0 to 4) have been used as the preservative in sulfiteless developers for high-contrast graphic arts purposes.[66]

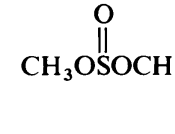
For general-purpose developers for photographic films and papers, at least 15 g/liter of a sulfite ester has been proposed[67] as a substitute for the conventional sodium sulfite. Suitable compounds include



1,2-ethylenesulfite



1,3-propylenesulfite



dimethylsulfite

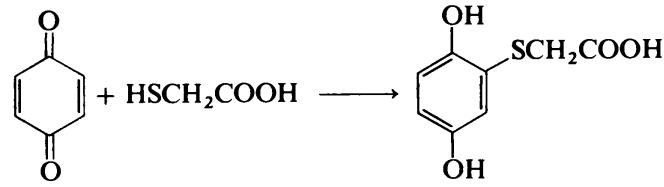
When combined with an alkali sufficient to give pH of at least 8, these compounds are suitable for liquid concentrates or combined developer-and-fixing solutions as well as working solutions of black-and-white photographic developers.

Amines may be reacted with sodium formaldehyde sulfoxalate or sodium formaldehyde bisulfite to produce sulfonates or sulfinates, such as, for example, sodium-β-hydroxyethyl-aminomethane sulfonate or sodium-β-hydroxyethylaminomethane sulfinate. These compounds are said to "act as preservatives and prevent formation of sludge during development."[68]

Compounds Other Than Sulfite

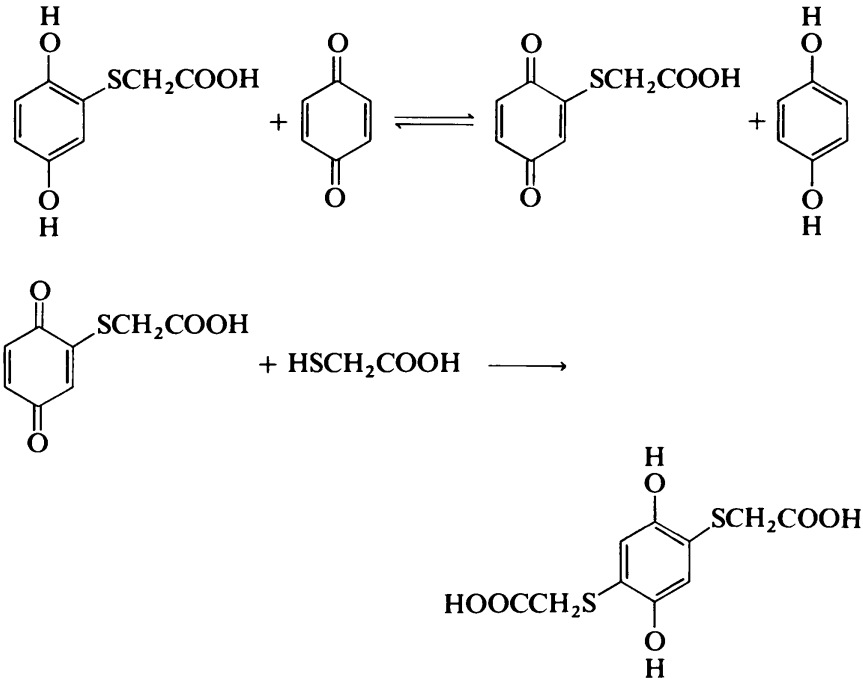
Compounds other than those yielding sulfite ions may be used to react with the oxidized forms of the developing agents. Certain organic compounds containing a mercapto group, —SH, will react with the oxidation products from benzene-type developing agents, thus preventing the coloration, staining, and accelerated degradation produced if these oxidized forms are

not removed.[69] According to J. M. Snell and A. Weissberger,[70] thioglycolic acid, $HSCH_2COOH$, reacts in a manner analogous to sodium sulfite:



quinone thioglycolic acid hydroquinone-α-thioglycolic acid

The hydroquinone-α-thioglycolic acid may react further to form a dithioglycolic acid compound. One method for this reaction might follow this path:



The removal of the quinone prevents the chain reaction that accelerates the oxidation of hydroquinone, and the solution is kept free from staining compounds. Many other mercapto compounds have been shown to react with quinones.[71,72] The addition of 1-phenyl-5-mercaptotetrazole to quinones has been extensively investigated.[73,74] Mercaptans add to quinone mono- and diimides.[75]

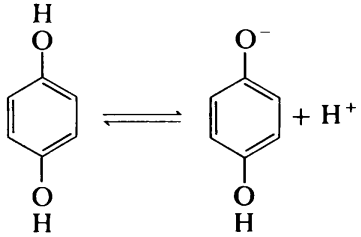
A monobath—that is, a single processing solution containing both developing agents, such as Phenidone and hydroquinone, and silver halide solubilizing compounds, such as thioglycolic acid—may suffer an unusually great loss of activity after use or upon standing. Quinone formed by aerial oxidation or reduction of silver ions may react with the very reactive mercapto compound rather than the sodium sulfite. The sulfite may not be present at all. The removal of the mercapto compound may upset the chemical balance of the monobath, making it difficult to secure the desired exhaustion characteristics for the processing bath.

Many other compounds have been proposed to protect sodium sulfite or the developing agent. Some of these are organic inhibitors of the chain reactions that occur in the developing solution.[76,77] An amino acid, such as cysteine, has been shown to be a good preservative in photographic solutions. Cysteine has been combined with sodium formaldehyde bisulfite in developing solutions that produce great contrast.[78] Arsenites, phosphites, and similar inorganic compounds may substitute for sodium sulfite or be present in addition to the normal amount of sulfite. Grape or cane sugar in a caustic developer solution was said to improve the keeping properties of the solution.[79] Sugars, such as sucrose or raffinose, as well as ascorbic acid and the ammonium salts of tartaric or citric acid, have all been combined in one developer for their preservative action.[80] Potassium ascorbic acid borate has been claimed to be more stable in alkaline solution than ascorbic acid.[81] Alcohols[82] or phenolic developing agents[83] inhibit the oxidation of sodium sulfite solutions. Small quantities of hydroquinone or other polyhydroxybenzenes are often used for their protective action in developers containing an active developing agent, such as Amidol. The combination of two developing agents often helps to increase the stability of the developing solution. Hydrazine or hydroxylamine acts as a preservative in color developers where the quantity of sulfite must be kept low. Many of these and other compounds may be used with low levels of sodium sulfite, or several may be present in the same solution.

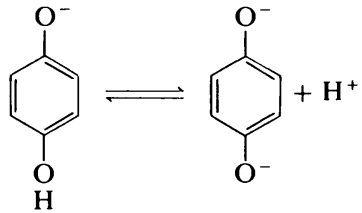
THE ALKALI

Organic developing agents are weak acids because of —OH groups, weak bases because of $-NH_2$ groups, or amphoteric—that is, contain both the acidic —OH and the basic $-NH_2$ groups. To be active as developing agents, these weak acids or bases should exist in the form that has the greatest electron availability. This form in acidic developing agents is the negatively charged ion, resulting from the loss of hydrogen ions. The most active form of the weakly basic developing agent is the uncharged molecule, which is the form most capable of transferring electrons.

Hydroquinone is an example of a weakly acidic compound that is inactive as a molecule for electron transfer. One proton (that is, a hydrogen atom minus one electron) may be lost from this compound to yield an ion with a single negative charge.

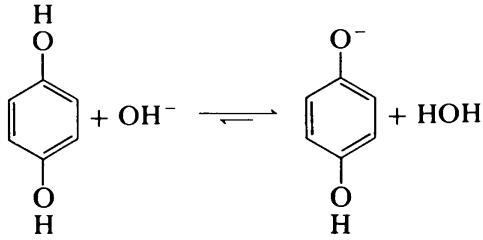


This ion may split off another proton to form the ion with two negative charges, the active developing agent of hydroquinone developers.



The ionization of hydroquinone will not occur unless there is an acceptor for the hydrogen ions that have been split off. Any tendency for the hydroquinone molecule to yield hydrogen ions in water solution is counteracted by a reverse tendency (as shown by the two equal arrows in the above equations) for the hydrogen ion to recombine with the hydroquinone ion, forming the un-ionized hydroquinone molecule. To prevent this recombination the hydrogen ions split off must be tied up in a molecule where they are not as free to react, as in a water solution.

One way to tie up the hydrogen ions is to add hydroxyl ions (—OH) to the water solution.



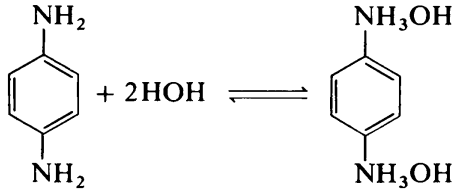
A molecule of water is formed, permitting the hydroquinone to form its ion. Two hydroxyl ions will convert the hydroquinone molecule to the doubly

charged form, which is believed to be the active form in the development of the latent image.

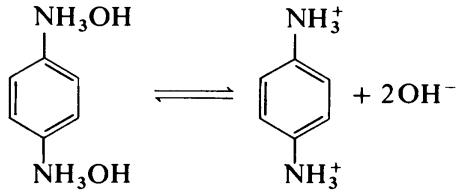
Compounds that furnish hydroxyl ions are called bases or alkalis. Hydroquinone requires the presence of an alkali if the compound is to act as a developing agent. The primary purpose of the alkali in developers is to convert the developing agent to a form, not necessarily ionic, that has the highest electron density. This is the form that can most easily transfer electrons during the amplification of the latent image.

Some developing agents are weak bases. They contain amino groups ($—NH_2$) that are capable of transferring electrons without needing to be in an ionic form as does hydroquinone. Some amino-containing developing agents, such as Amidol or Metol, are capable of electron transfer even under mildly acidic conditions. Even the weakly basic developing agents are more active in alkaline solution. This increase in activity must indicate that a form more suitable for electron transfer is present under the alkaline conditions.

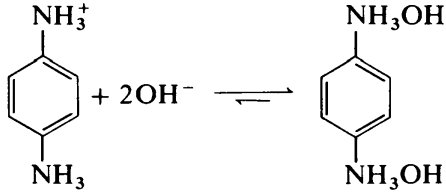
para-Phenylenediamine is a basic developing agent having two $—NH_2$ groups para to each other on the benzene ring. In water solution this compound adds two molecules of water,



forming uncharged $—NH_3OH$ groups. This molecule may then give off hydroxyl ions.



The doubly charged positive ion has a poorer electron transfer ability than the uncharged molecule. If we add more OH^- ions to the solution—that is, more alkali—the concentration of the positively charged ion is decreased.



More uncharged molecules are formed in alkaline solution, making more of the most active form available for electron transfer.

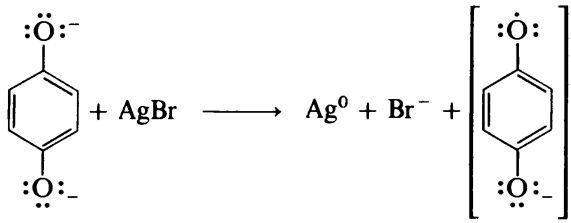
With basic developing agents the alkali helps to prevent ionization, whereas acidic developing agents are ionized by it. With developing agents containing both hydroxyl and amino groups, such as *p*-aminophenol, the presence of an alkali helps each group to assume a form most capable of electron transfer. But an alkali does not speed the developing action of a metal-ion developer, such as one containing ferrous oxalate. Ferrous oxalate developers have an activity that is independent of the pH of the solution, usually from pH 4 to 7. Metal-ion developers usually require acidic conditions, as the metal ions are precipitated from alkaline solutions.

The threshold of development, i.e., the pH value at which the first discernible density was obtained, was measured by Malon H. Dickerson[84] for a number of organic developing agents. As tabulated below, Amidol is capable of development at pH 4.0 but hydroquinone requires a pH of 10.0. In practice, developers require sufficient alkali to exceed these pH values if development of normal contrast and density is to be achieved in a reasonable time.

Developing Agent*	Threshold of Development, pH
Amidol	4.0
Phenidone (2.0 g/liter)	6.0
p-Phenylenediamine	6.25
Metol (4.0 g/liter)	7.25
Pyrogallol	8.0
Chlorohydroquinone	8.5
Bromohydroquinone	8.5
Glycin	9.0
p-Aminophenol	9.35
Catechol	9.5
Hydroquinone	10.0

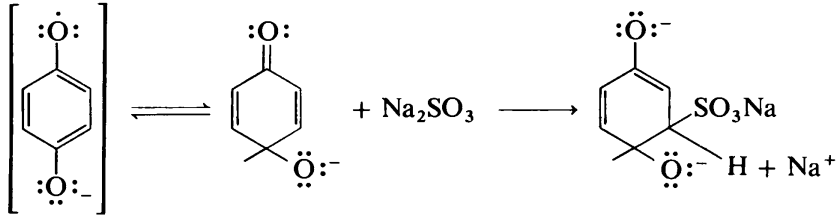
* Each developing agent was tested at a concentration of 0.1 of the molecular weight of the compound in a liter of water unless solubility limited the amount to that shown in the table. Development time did not exceed 60 sec at 90°F.

The alkali is needed not only to secure the most active form of the developing agent but also to maintain it during the development of the latent image. According to T. H. James and G. C. Higgins,[85] the reactions of a sulfite-containing hydroquinone developer may be represented as

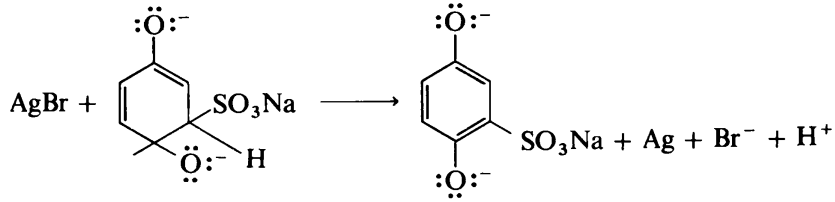


The doubly charged negative hydroquinone ion transfers one electron to the silver ion of silver bromide, forming metallic silver, a bromide ion, and a form of hydroquinone that has lost one electron (the semiquinone).

In the presence of sodium sulfite this hydroquinone intermediate reacts to form a sulfonate.



This intermediate sulfonated ion then loses another electron to the silver bromide.



Hydroquinone monosulfonate and metallic silver result. Hydrogen ions and bromide ions are also formed as a result of the reduction of the silver ion.

If the acidic products of development were allowed to build up, the reduction of silver ions would be slowed down. The acidic condition would produce the hydroquinone molecule, which is less capable of electron transfer than the hydroquinone ion. The presence of sufficient hydroxyl ions in the developer insures that the hydrogen ions are made to form water molecules, maintaining the developer activity of the hydroquinone without change.

During development the alkali must neutralize the acid by-products of the formation of the silver image. The ability of an alkali to resist a change in the pH of the solution is called its buffering capacity.[86] Buffer solutions are formed by the interaction of weakly ionized acids with their salts.[87] This

buffering ability of an alkali is important because local concentrations of acid may be formed within the silver halide emulsion layer, especially in areas of considerable light exposure. Such localized amounts of acid may be sufficient to slow development in those areas where they are formed. In areas of low light exposure of the photomaterial, the effect would be negligible.

In some developers the slowing of development by the restraining acid might be overcome by extending the time of development. However, in combined developers and fixers (monobaths) the less active developing agent may not be able to act fast enough before being overwhelmed by the attack of the fixing agent upon the silver halide grain. Fixing agents, such as sodium thiosulfate, work about as well in acid as in alkaline solution, so a local concentration of acid in any of the emulsion layer would not slow its activity.

Some alkalis or combinations of alkaline compounds have good buffering action during development. Considerable amounts of these alkalis are needed for the formation of high density and high contrast in the image. However, alkalis that have weak buffering ability are also of use for making developers. Developers containing poorly buffering alkalis are restrained by the production of acid in areas of considerable light exposure of the emulsion layer. The growth of image density is limited in these areas of high exposure, but the growth of image density is not affected in areas of low image exposure. Unlike a well-buffered developer, a poorly buffered developer decreases the density differences between the areas of considerably different exposure. This type of restricted image formation is called compensated development. Compensating developers produce fine-grain images because the image is essentially being underdeveloped in high-exposure areas as compared to the results obtained from a buffered developer.

Activating and maintaining the most active form of the developing agent in solution is the primary purpose of the alkali, but alkalis have many other effects in developers. One effect is to neutralize the acidity of those developing agents that are supplied as acid salts. Basic developing agents in the solid form, such as *p*-aminophenol, *N*-methyl-*p*-aminophenol, and *p*-phenylenediamine, are very unstable in air and not very soluble in water. This type of developing agent is usually reacted with a strong acid, such as hydrocholric or sulfuric acid, to form a salt of increased stability in air and greater solubility in water.

The first action of the alkali of a developer is to neutralize this acid from the developer salt. The liberated free base is not very soluble under weakly alkaline conditions and may precipitate from the solution. However, the addition of further alkali will dissolve the precipitated developing agent. Unfortunately, if the precipitation occurs in a solution containing sulfite, the free base of the developing agent does not want to redissolve. E. J. Wall[88,89]

has reported that the precipitation of the free developing agents from alkaline solution is particularly noticeable with *p*-aminophenol hydrochloride but may occur in more or less degree with Metol, Ortol, triaminophenol hydrochloride, *p*-phenylenediamine hydrochloride, and bromo- or chlorohydroquinone. If a strong alkaline solution is used, the precipitation stage may be so brief as to be unnoticed.

Alkalis help the gelatin to swell so that the developing agent may penetrate the emulsion layer to the silver halide grain. The function of sodium carbonate in a developing solution was once attributed to the opening of the pores of the gelatin.[90] The gelatin capsule surrounding and binding each grain would be softened also. After the developing reaction has occurred, alkali helps to decompose the oxidation products of the developing agent. These oxidized products may in some cases inhibit the further reaction of the developing agent, so their removal helps speed the formation of the silver image.

The Alkaline Compounds

W. T. Hanson, Jr., found that "almost all alkalis had practically identical effects if compared at the same pH."[91] The concentration of the hydroxyl ions, not the substance that supplied them, was the important condition. Although alkaline compounds in some developers may be interchangeable from purely chemical equivalence,[92,93] in practice one alkali may be preferable over another. Sometimes this choice is dictated by the other ingredients in the developer or the effect of the retained alkali as the processed emulsion layer is immersed in the acid baths that stop development and make the image permanent. The choice of an alkali for high-pH developing solutions is limited to caustic compounds because other alkalis are not suitable. The alkalinity of the solution is one of the factors that determines the rate of development. Other factors include the nature and concentration of the developing agent, the nature and concentration of other agents in the solution, the temperature of solution, and the nature and the exposure of the photographic material.[94] In contrast with the almost universal use of sodium sulfite for the developer preservative, a considerable number of alkalis have found practical use in developer compositions.

Caustic Alkalis

Water exists primarily as a molecule, HOH. A very small number of water molecules ionize to give hydrogen ions and hydroxyl ions, equal in number. The number of such ions present in water cannot exceed a definite value, which is a constant. If one ion common to water is added to water, then the other ion must be decreased in quantity to maintain the constant. When an

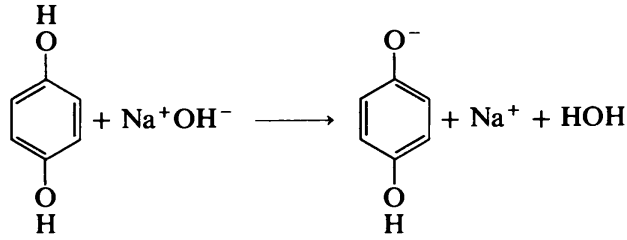
acid—that is, H^+—is added to water, some of the hydroxyl ions will combine with the added H^+ to form water molecules. An excess of hydrogen ions will still be present, however, and the solution will be acidic. To counteract this drop in pH (increase in H^+), hydroxyl ions may be added. The resulting formation of water molecules removes some of the hydrogen ions, and the pH of the solution will rise.

A primary source of hydroxyl ions in photographic processing is the caustic alkalis: sodium hydroxide (NaOH), potassium hydroxide (KOH), and lithium hydroxide (LiOH). These compounds are strongly basic substances because they exist in solution as the ions; that is, all of the hydroxyl ions are readily available.

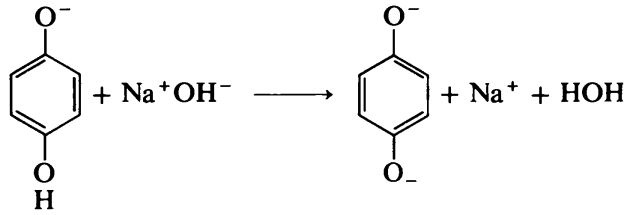
$$NaOH \longrightarrow Na^+ + OH^-$$

The vigorous action of so many hydroxyl ions has given these hydroxides the name of caustics.

One action of the caustic alkalis is to form salts, sometimes called phenolates, with acidic organic developing agents as with hydroquinone. In solution the phenolate is ionized so that the result of the reaction between hydroquinone and sodium hydroxide may first be represented by



Another hydroxyl ion may then react to form the doubly charged hydroquinone ion.



In alkaline solutions the acidic hydrogens of the hydroquinone are combined with the hydroxyl ions to form water molecules. The hydroquinone exists as the fully ionized form, the form that is the most capable of transferring electrons to the latent image.

Caustic alkalis yield high-pH solutions, around pH 13, but considerable quantities must be present to maintain these high-pH conditions during development. When a large quantity of caustic is present in a developer, the development is most rapid, yielding high densities and contrasts. However, high concentrations of caustic alkali, especially if excessive, increase non-image development (fog), soften the gelatin of the emulsion layer,[95] and may injure the skin of human beings. High-pH caustic developers are unstable because of the high reactivity of the developing agent, even in the presence of considerable preservative.

Sodium hydroxide is available as easy-to-dissolve granules, pellets, and other forms. The white opaque pieces of the compound absorb carbon dioxide and water from moist air, forming carbonate.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Potassium hydroxide is similar in appearance and properties to the sodium compound. Both compounds should be kept in tightly closed containers but not glass-stoppered. Lithium hydroxide is less soluble than the other caustics. It may be available as a white powder that does not take up water from the air. Containers of lithium hydroxide must still be able to prevent this compound from reacting with carbon dioxide from the air. Caustic alkalis are extremely corrosive, especially sodium hydroxide, and contact with the skin or eyes should be guarded against.

Carbonate Alkalis

The sodium, potassium, lithium, and ammonium carbonates are widely used for alkalis in developers. The sodium salt is the one most commonly found in developer formulations, but the potassium salt, because of its higher solubility, is the carbonate used for concentrated developers. A salt is the result of the neutralization reaction between an acid and a base. Sodium carbonate might be obtained from a reaction between a strong base, sodium hydroxide, and a weak acid, carbonic acid.

$$2NaOH + H_2CO_3 \longrightarrow Na_2CO_3 + 2HOH$$

How can a salt act as an alkali? Sodium carbonate acts as a base because when the solid compound is dissolved in water, the salt reacts with water, an action called hydrolysis.[96,97]

$$Na_2CO_3 + HOH \longrightarrow Na^+ + OH^- + Na^+ + HCO_3^-$$

The carbonate is split by hydrolysis into the fully ionized sodium hydroxide and an acidic bicarbonate ion (HCO_3^-). The bicarbonate ion effectively removes the H^+ from any independent activity. Most of the carbonate is

still in the form of the undissociated carbonate molecule. However, as soon as the hydroxyl ion is used, more carbonate dissociates to form more hydroxyl ion and bicarbonate ion. Only a very small amount of the active alkali, the hydroxyl ion, is present at any one time, but a reservoir of alkali is available through the hydrolysis reaction.

The pH of sodium carbonate at different concentrations has been determined by F. S. Nakayama.[98]

Concentration of Na_2CO_3 (fraction of mol wt)	pH of Solution
1	12.13
0.1	11.62
0.01	11.10
0.001	10.54
0.0001	9.85
0.00001	8.98

The action of the carbonate-bicarbonate system keeps the free alkali level low but maintains the alkali activity approximately at a constant level throughout the action of the developer. The pH attainable with carbonate developers is around 10 to 11.5, considerably below that of hydroxide developers where all the hydroxide ion is immediately available. But carbonate developers do not soften the gelatin of emulsion layers as much as hydroxide developers and they are not as injurious to human skin. The high salt content due to the carbonate tends to keep the emulsion layer from swelling.

Sodium carbonate exists in three forms[99]:

Form	Formula	wt % Carbonate
The anhydrous (or desiccated)	Na_2CO_3	100%
The monohydrate	$Na_2CO_3 \cdot H_2O$	85%
The decahydrate	$Na_2CO_3 \cdot 10H_2O$	37%

The anhydrous crystals are 100% sodium carbonate, the desiccated powder 98% sodium carbonate. The monohydrate contains one part of sodium carbonate and one part of water, making it necessary to use $1\frac{1}{6}$ times as much of the monohydrate as the anhydrous (17% more of the monohydrate). The decahydrate contains one part of carbonate to 10 parts of water; by weight

the compound is almost two-thirds water. One hundred and seventy percent more of the decahydrate is needed as of the anhydrous form for an equal concentration of carbonate.

The decahydrate with its 10 molecules of water is relatively unstable, tending to lose some of this water of crystallization (effloresce) in dry air or to absorb water from damp air. The decahydrate may also absorb carbon dioxide from the air to form sodium bicarbonate ($NaHCO_3$), which is of little value for developers. E. J. Wall[88] reported that after 13 days' exposure to air, the decahydrate of sodium carbonate may contain as much as 15 to 20% of the bicarbonate compound.

Desiccated sodium carbonate is now readily available. This compound, according to J. I. Crabtree and G. E. Matthews,[100] rarely absorbs sufficient water to have any appreciable photographic effect in developers. Its caking tendency during the mixing of the developer is not greater than that of the monohydrate. Sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is a compound found in nature. This compound, called trona, contains one molecule of sodium carbonate and one molecule of sodium bicarbonate with about 16% by weight of water. Methods have been patented to produce sodium carbonate–sodium bicarbonate compounds without the water or with varying proportions of the carbonate and bicarbonate.[101] The natural sodium sesquicarbonate as well as the synthetic compounds may be used in developing solutions.

Anhydrous potassium carbonate (K_2CO_3) in many developers may be substituted, weight for weight, for the anhydrous sodium carbonate. S. E. Sheppard and F. A. Anderson[102] could find no detectable photographic difference when an Elon-hydroquinone contrast developer contained either the potassium or sodium salt in molecular equivalent quantities. In other developers this relationship may also hold; in yet others, different photographic results may be obtained. Potassium carbonate is very soluble, suggesting its use for concentrated developer solutions. It absorbs water from the air very readily, becoming moist and preventing carbonate dust from floating in the air. Like any of the carbonates, it has a tendency to react with the carbon dioxide of the air. Potassium carbonate is more costly than the sodium salt and for this reason is not widely used.

The monohydrated sodium carbonate is probably the most commonly used carbonate in developers. It is relatively stable to the effects of the air, more so than the decahydrate, and does not cake badly during the preparation of the developer solution. It is necessary to use 1.17 times as much of the monohydrate as of the anhydrous for equal alkaline effect.

The use of carbonates in developers may produce blisters in the emulsion layer of the photographic material when this material is transferred from the alkaline developer to any acid afterbath, such as an acid stop bath or acid

fixing bath. This tendency is increased during processing at other than normal room temperatures, especially under high-temperature processing conditions. The carbonate still retained in the emulsion layer after development reacts with the acid of the afterbaths to produce carbon dioxide gas bubbles, which may then rupture the gelatin of the emulsion layer.

Borate Alkalis

Borate alkalis do not soften gelatin or attack the human skin in the same way as do the caustic alkalis; they do not release any gas, as do the carbonates, when the alkaline developer is neutralized in an acid fixing bath. Borates do not cause the precipitation of aluminum sulfite in fixing baths that do not contain boric acid. But borates are useful for developer alkali when the solution pH is around 10. These compounds should not be used with developing agents having two hydroxy groups ortho to each other, as in catechol or pyrogallol. Borates react with *o*-dihydroxybenzene compounds to produce a reaction product that has very low developing action.

Borax, $Na_2B_4O_7 \cdot 10H_2O$, is the common name for sodium tetraborate, an alkaline compound used in the preparation of low-contrast, fine-grain developers. Borax may be written $(NaBO_2)_2 \cdot B_2O_3$, which shows the boric anhydride that limits the alkalinity possible from borax. The compound itself does not have inherent fine-grain properties, but the mildness of the alkaline activation produces a developed image that possesses such characteristics. Borax acts as a buffer; that is, it maintains a reservoir of alkali but delivers only small quantities of hydroxyl ions at any one time. The alkalinity of the developer is maintained relatively unchanged until all of the borax has been neutralized.

The formation of hydroxyl ions by the hydrolysis of borax is a complex reaction. According to Richard B. Willcock,[103] the first reaction is

$$Na_2B_4O_7 + 3H_2O \longrightarrow 2NaBO_2 + 2H_3BO_3$$

which is followed by

$$NaBO_2 + 2H_2O \longrightarrow Na^+ + OH^- + H_3BO_3$$

Only 0.3% is said to be hydrolyzed in a solution containing 0.1 mol wt in 1000 ml. Borax provides a pH of 9.2, a much lower value than either the carbonates or hydroxides, and this limits its usefulness to low pH developers.

Borax has low solubility in water. The limited amount of borax that may be used in developers means that the pH of the solution is relatively low, yielding a solution with limited activity. Forty grams of borax are required to give the same activity as 4 g of desiccated sodium carbonate in a given developer, according to J. I. Crabtree and G. E. Matthews.[104]

When borax is fused with caustic soda (sodium hydroxide), sodium metaborate ($NaBO_2 \cdot 4H_2O$) is formed. This reaction may be written, according to the U. S. Patent of Harold D. Russell,[105]

$$\underset{\text{borax}}{Na_2B_4O_7 \cdot 10H_2O} + \underset{\substack{\text{sodium}\\\text{hydroxide}}}{2NaOH} \longrightarrow \underset{\text{sodium metaborate}}{2Na_2B_2O_4 \cdot 4H_2O} + \underset{\text{water}}{3H_2O}$$

Sodium metaborate is sold under the trade name of Kodalk. The addition of caustic alkali to a developing solution containing borax is said by L. P. Clerc[106] to produce sodium metaborate in the solution. Harold D. Russell[107] claimed that the proportion of the borax to the caustic alkali is approximately 2:1. Kodalk has alkaline properties between those of borax and carbonate. The compound is very soluble in water (33% at 66°F) and does not cake during mixing of developer. No gas is released when Kodalk is neutralized in an acid stop or fixing bath, greatly minimizing the danger of blister formation in the gelatin. Scums are not as readily formed in fixing baths containing potassium alum when the developer contains sodium metaborate rather than sodium carbonate. The carbon dioxide of the air may act upon sodium metaborate, either solid or in solution, gradually forming borax and sodium carbonate.

Boric acid is often combined with borax or sodium metaborate to form buffered borate developers.[108] The boric acid neutralizes some of the hydroxyl ions formed by the hydrolysis of the meta- or tetraborate. The number of undissociated ions is decreased. The pH of the solution is lowered, but the solution has greater power to resist pH changes due to any reactions occurring during development.

The pH of various solutions of the borate alkalis and boric acid has been given by Pierre Glafkides[109] as follows:

	Concentration			
	2%	4%	6%	8%
Borax	pH 9.4	pH 9.6	—	—
Sodium metaborate	pH 10.4	pH 10.6	pH 10.7	pH 10.8
Boric acid	pH 4.5	pH 3.9		

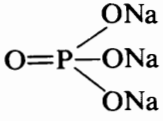
Phosphate Alkalis

Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$), often called tribasic sodium phosphate, occurs as colorless crystals that easily lose some of their water of crystallization. This may lead to some uncertainity as to the alkali content of

various samples of the compound. In solution trisodium phosphate (often abbreviated to TSP) forms sodium hydroxide and disodium phosphate.

$$Na_3PO_4 + H_2O \longrightarrow Na^+ + OH^- + Na_2HPO_4$$

Trisodium phosphate may be written in the following form, which shows its character more clearly:



The alkali characteristics of this compound were studied as early as 1896.[112] If trisodium phosphate is not available, the mixing of disodium phosphate, if available, with sodium hydroxide would produce the tribasic salt.

In developers trisodium phosphate provides pH values between those of the carbonates and the caustic alkalis. The alkalinity of trisodium phosphate developers is quite high, around pH 12. Yet, this alkali does not have as much gelatin-softening effect as do the caustic alkalis in developers at pH 13. Considerable quantities of trisodium phosphate may be used, and this salt content of the developer may also help keep the emulsion layer from swelling. Trisodium phosphate developers containing a high sodium sulfite concentration have been reported to increase in activity when diluted.[110,111]

Trisodium phosphate has found only limited use, however, because it reacts with the alum in an acid-hardening fixing bath to form aluminum phosphate. Aluminum phosphate has low solubility in the fixing bath, depositing as an objectionable scum on the surface of the emulsion layer of a photographic material. Although trisodium phosphate is useful only when a nonhardening fixing bath follows the developer, this salt has many attractive properties for photoprocessing systems that do not utilize hardening afterbaths.

The Sulfite Alkalis

Sodium sulfite is a weakly alkaline salt that is capable of acting as the sole alkali for developing agents with amino groups, as, for example, Metol or Amidol. Sodium sulfite is an alkali because it hydrolyzes in solution to produce sodium hydroxide.

$$Na_2SO_3 + HOH \rightleftharpoons Na^+ + OH^- + Na^+ + HSO_3^-$$

Most of the sodium sulfite remains in the undissociated molecule and the amount of hydroxyl ion formed is low. However, this amount of alkali is sufficient to activate some developing agents for fine-grain developers. A

number of developer formulas of this type have found important photographic usage.

Other compounds have been reacted with sodium sulfite in developers to produce sufficient alkali for more energetic development. Acetone,

$$CH_3—CO—CH_3,$$

is a colorless liquid with a distinctive odor. It is a volatile, inflammable organic liquid that mixes in all proportions with water. Acetone reacts with sodium sulfite, forming acetone bisulfite and sodium hydroxide.

$$CH_3—CO—CH_3 + Na_2SO_3 + HOH \longrightarrow (CH_3—CO—CH_3 \cdot NaHSO_3) + Na^+ + OH^-$$

The amount of hydroxyl ion produced is then capable of activating developing agents, such as hydroquinone or pyrogallol, that require solutions of about pH 10. Acetone-containing developers were studied by A. and L. Lumière and A. Seyewetz.[113–116] T. Thorne Baker[117] has pointed out that "Great care must be exercised between development and fixing. If the plate be put straight into the fixing bath, the film will become marked with large spots or streaks. Owing to the greasy nature of the acetone, the negative must be held under a running tap for some moments before immersion in the hypo; the film is thus rid of acetone and its by-products with the developer, and fixing takes place readily."

Formaldehyde, CH_2O, is a very pungent gas with an irritant effect on the eyes and nose. This compound is usually supplied as formalin, a solution of about 400 g of the compound in a liter of water. Some methyl alcohol may also be present in formalin. A solid form of formaldehyde is called paraformaldehyde—sometimes still referred to as trioxymethylene—a whitish powder of about 95% formaldehyde and 5% water combined to form large polymeric molecules.[118] Paraformaldehyde is not very soluble in water but does break down in alkaline solution to provide formaldehyde.

Formaldehyde in the presence of sodium sulfite reacts to produce an alkali.[119] According to J. F. Ross and J. I. Crabtree[120] sodium hydroxide results when sodium formaldehyde bisulfite is formed.

$$HCHO + Na_2SO_3 + HOH \longrightarrow (HCHO \cdot NaHSO_3) + Na^+ + OH^-$$

Other aldehydes may be used that do not have all the objectionable properties of formaldehyde.

The use of formaldehyde with sulfite to provide an alkali for developers has been limited, particularly because of the tendency to produce fog. Formaldehyde is a developing agent itself.[121,122] It was noted as early as 1912[123] that hydroquinone developers with low sulfite and formaldehyde produced high-contrast images, especially suitable for reproducing line images. A

two-solution hardening developer was proposed by H. Parker and J. I. Crabtree[124] utilizing the alkali produced by the reaction between formaldehyde and sodium sulfite. Formaldehyde tans or hardens the gelatin of the emulsion layer.[125,126]

Ammonia Alkalis

Ammonia, NH_3, is a pungent, irritating gas. It dissolves in water to form ammonium hydroxide, an alkali capable of activating developing agents.

$$NH_3 + HOH \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Unfortunately, the reactions are readily reversible, and ammonia gas is easily given off from the solution. Developers made with ammonia are not stable, as the loss of the ammonia gas continuously decreases the strength of the alkali. This loss of ammonia gas increases as the temperature of the solution is increased. The salts formed by the reaction of ammonium hydroxide with acids are also relatively unstable. Some salts, such as ammonium sulfite and ammonium carbonate, have found specific uses in specialized developers.

Solutions of ammonia dissolve silver chloride, and, to a lesser extent, silver bromide. The dissolved silver ions in the silver ammonia complex may be easily reduced to metallic silver by the developing agents in the developer. This action usually produces increased nonimage density, sometimes in the form of a silver deposit on the surface of the emulsion layer. Metallic silver may also be deposited on the immersed surfaces of the container holding the developer. Such an indiscriminate loss of silver from the emulsion means that the developed image will not have had the amplification that other less-solubilizing alkalis can produce.

Ammonia was the alkali in the very first alkaline developer ever used in photography. In 1862 Major C. Russell[127] perfected an ammonia-pyrogallol formula for developing collodion dry plates, although the use of ammonia for fuming dry plates is generally credited to H. T. Anthony[128] of New York. The use of ammonia in liquid form was suggested by T. M. Leahy in 1862.[129] Collodion plates had an emulsion high in silver iodide which is little solubilized by the ammonia. The replacement of the collodion–silver iodide plate by the gelatin–silver bromide plate made the ammonia-containing developer less satisfactory than other alkaline developers. Today, ammonia finds only very limited application in developers.

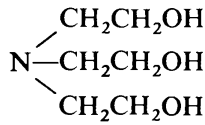
The volatility and silver solvency of ammonia may be decreased by replacing one, two, or three of the hydrogens of ammonia by carbon-containing groups. Replacing one hydrogen produces a primary amine; replacing two gives a secondary amine; and replacing three forms a tertiary amine. For

photographic purposes one or more of the hydrogens are replaced by small alkyl groups, such as methyl (CH_3—) or ethyl (CH_3CH_2—), or substituted alkyl groups, such as the ethanol group, $HOCH_2CH_2$—. Most amines still possess some odor that may be objectionable. Amines also solublize silver chloride and silver bromide but may not deposit metallic silver as readily from solution as does ammonia. Depending on the nature of substituents on the nitrogen, aromatic amines exhibit a basicity ranging from about pH 7 to pH 12.[130]

Trimethylamine, $(CH_3)_3N$, was used as early as 1898 as an alkali for developers. In 1899 the Lumière Brothers and A. Seyewetz[131,132] reported that methylamine, CH_3NH_2, and ethylamine, $CH_3CH_2NH_2$, were very energetic alkalis in a hydroquinone developer but the dimethylamine, $(CH_3)_2NH$, and the diethylamine, $(CH_3CH_2)_2NH$, were less energetic in equal quantities. Trimethylamine was the only one found to give fog-free images, producing developers more active than those containing carbonate alkalis. These developers were said not to attack the gelatin or injure the fingers. Trimethylamine would produce alkali by interaction with water, much in the same fashion as ammonia.

$$(CH_3)_3N + HOH \longrightarrow (CH_3)_3NH^+ + OH^-$$

In 1932 Merle L. Dundon[133] patented tertiary amines containing one or more hydroxyethyl or alkyl groups. Triethanolamine was used as the alkali in sulfite-containing developers.



triethanolamine

The sodium salt of triethanolamine, as claimed by H. D. Russell,[134] may be the alkaline component of the developing solution or may be combined with another alkali, such as sodium metaborate. The sulfite salts of triethanolamine or other hydroxyalkylamines may replace both the usual alkali and the preservative.[135,136] Triethanolamine and triethanolamine sulfite were used in the same solution. Much more recently, 2-aminoethanol and 2-aminoethanol–sulfur dioxide addition product were used as the alkali, preservative, and solvent for a liquid photographic silver halide developer concentrate.[137] 2-Methylaminoethanol hydrobromide may serve as a development restrainer.

Triethanolamine was suggested in 1937 by Maurice Ney[138,139] for fine-grain development. Triethanolamine is weakly alkaline, does not attack the gelatin or film base, and is odorless and nonirritating (unlike acetone). The developer containing it was said not to lose its alkalinity as do ammonia developers. A. Seyewetz,[140,141] however, did not like the high viscosity of

triethanolamine, preferring an acetone-sodium sulfite-pyro developer for fine-grain development. The tertiary amines do appear to have desirable properties for photographic uses. A tertiary amine, such as diethylaminoethanol, which this writer has found to be especially useful, minimizes the swelling of the gelatin layers. Tertiary amines are still somewhat volatile, may possess an undesirable odor, and require considerable quantities for effectiveness. These undesirable qualities were said to be overcome when amines containing two or more amino groups, such as ethylenediamine or diethylenetriamine, were present in the developing solution. Improved developer stability was claimed.[142]

One property of ammonium compounds and amines is their effect as development accelerators, producing greater image density during the initial stages of development than do developers without the amine. As does ammonia, amines tend to solubilize silver from the grains of the emulsion but, unlike ammonia, amines do not as readily deposit silver on every available surface. Some of the silver solubilized by the amine may be used for physical development of the silver image, in many cases producing greater image graininess. Amines are especially useful for combined developer-fixers where rapid image formation is vital if emulsion speed losses are to be minimized.

Certain aminoalkyl-substituted heterocyclic compounds were said[143] "to provide a black and white and color developer having an increased rate of development so that developing time is substantially decreased to less than half of the normal time without loss of contrast and speed." *m*- or *p*-Xylylene diamine reduced development time from 16 to 10 min in a black-and-white developer.[144] A saving of 15 to 20% in development time was found by Fritz Dersch and Newton Heimbach[145] when large amounts of urea were in the developer. Accelerated development times were also reported for phenoxyalkylamines,[146] negatively substituted (—Cl, —Br, $-NO_2$) benzene with alkylamino substitutions,[147] as well as the benzene derivatives without the negative groups,[148] and other amines.[149] Guanidine carbonate and trimethylbenzylammonium hydroxide have been used in negative developers as sole alkalis.[150,151]

Sodium dicyanamide, $NaN(CN)_2$, was found by Grant M. Haist, James R. King, and Lance H. Bassage[152,153] to produce very long, loosely packed silver filaments when this compound was present in a Metol-hydroquinone developer (Kodak D-76 developer). Increasing amounts of sodium dicyanamide in the developing solution caused progressive increases in both emulsion speed and contrast of the silver image.

The Practical Equivalence of Alkalis

The pH of the developer determines the extent of the activation of the developing agent. In some cases it might be possible to substitute one alkali for another and still achieve similar photographic results. When extremely high-pH developers are required, the caustic alkalis are the only possible choice, as these compounds are almost entirely in the state of hydroxyl ions. It is impractical to use the caustic alkalis for low-pH developers. So little of the caustic compound would be required that the developer alkali would be soon exhausted by use. For moderate-pH developers, however, more than one alkali might provide similar photographic results.

The equivalence of the hydroxides and the carbonates in developers was studied by A. and L. Lumière and A. Seyewetz[154] in 1906. The relative quantities of the alkalis needed to give equal photographic effect was determined for different developing agents, but the same composition was not used for all of the developers. Their results are tabulated below.

Developing Agent	Sodium Hydroxide	Potassium Hydroxide	Sodium Carbonate Anhydrous	Potassium Carbonate Anhydrous
Chemically equivalent quantities	10	14	26.5	34.5
Hydroquinone	10	14	96	75
Pyrogallol	10	14	34.2	32.4
Metol	10	14	34.2	28.3
Glycin	10	14	122.5	74.5

The first line lists the quantities of each alkali that would be predicted on the basis of their equivalent weights. The experimentally determined quantities are listed on the basis of 10 parts of sodium hydroxide. For the hydroquinone developer, 10 g of sodium hydroxide is the alkali equivalent in a developer containing either 14 g of potassium hydroxide, or 96 g of anhydrous sodium carbonate, or 75 g of anhydrous potassium carbonate.

The relative activating powers of various alkalis have been determined by A. Seyewetz[155,156] for the reduction of equal quantities of silver bromide in a hydroquinone developer. Seyewetz did not find a list of equivalents that would be valid for solutions of different developing agents. For the hydroquinone developer, and giving lithium hydroxide, the most powerful, an

arbitrary value of 1, the quantities of various alkalis needed for equal silver reduction are as follows:

Lithium hydroxide	1.0
Sodium hydroxide	2.5
Sodium trisodium phosphate	26.3
Potassium hydroxide	4.5
Potassium carbonate	16.9
Ammonia	4.8
Sodium carbonate	16.9
Triethanolamine	15.4
Sodium metaborate	19.1

The Lumières and Seyewetz in 1906 did not use a fixed developer composition to determine their alkali equivalents. In their investigation of alkalis, J. I. Crabtree, G. E. Matthews, and H. D. Russell[157] used a single developer composition: 5.0 g of each developing agent, 37.5 g of sodium sulfite (anhydrous), and 1.5 g of potassium bromide in a liter of water. The amount of each alkali was varied until as similar photographic results as possible were obtained. As the control developer, 25 g of sodium carbonate was used to produce a developer pH of 9.5. The quantities of the alkalis did not vary appreciably when different developing agents were present, unlike the results obtained by the Lumières and Seyewetz. The results from the study of alkalis in a fixed developer composition are as follows:

Sodium Hydroxide	Potassium Hydroxide	Sodium Carbonate Anhydrous	Potassium Carbonate Anhydrous	Tribasic Sodium Phosphate
10	15	130	130	100

In a pH 9.0 developer containing 2.0 g of Elon and 5.0 g of hydroquinone with 100 g of sodium anhydrous sulfite in a liter of water, equal densities and fog were produced by alkalis in these proportions.

Sodium Hydroxide	Sodium Carbonate Anhydrous	Kodalk	Borax
1	3	5	20

In this lower-pH developer three times as much carbonate as hydroxide is required for equal photographic effect. In the previous, higher-pH developer, containing a single developing agent, 13 times as much carbonate as hydroxide was required.

The equivalence of alkaline substances, although in some cases interchangeable in practice, is directly related to the pH of the specific developer composition and to the nature of the developing agent or agents in the solution. (See Figure 2.) It is thus impossible to generalize upon the equivalence of certain alkalis until the nature of the developer is specified. Substitution of one alkali for another may be possible on the basis of alkaline equivalence, but developer properties may still differ in some respects because of some of the other specific properties of the alkali. R. B. Willcock[158] has said, "The energy of sodium carbonate as an accelerator is limited by its solubility, and only in exceptional circumstances has it a reactive energy approaching the

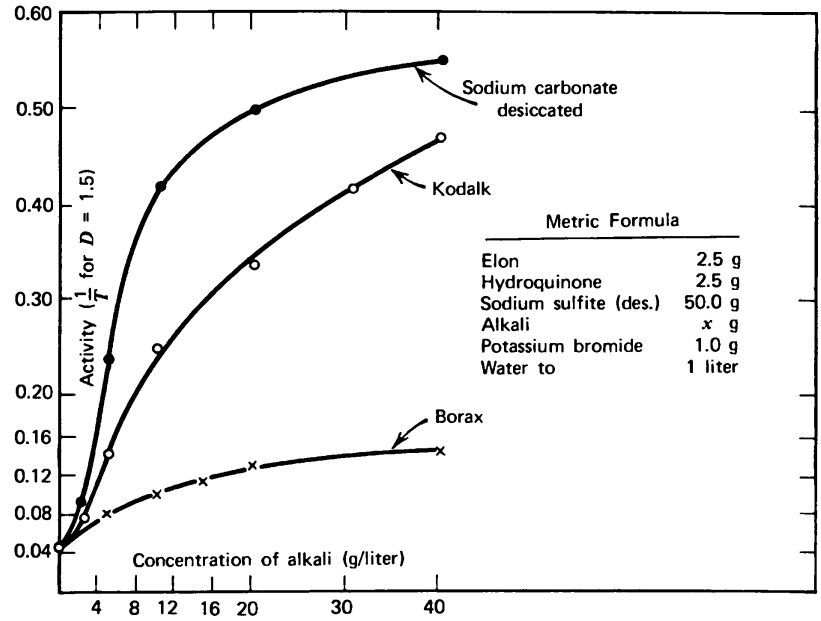


Figure 2. Comparative activity of alkalis in an MQ developer. Graphical representation of the variation of the photographic activity of a developing solution with different concentrations of borax, Kodalk, and sodium carbonate. The activity is expressed on the vertical line as the reciprocal of the time of development to produce a density of 1.5; the concentration of the three alkalis is shown on the horizontal line. The curves indicate that the developing activity of a solution containing 40 g of borax is the same as a solution with 4 g of carbonate. (J. I. Crabtree and G. E. Matthews, *Photographic Chemicals and Solutions*, Am. Photo. Pub. Co., Boston, 1938, p. 120)

caustic alkalies. The intention of these notes is to show that molecular alkaline equivalents are misleading when used to compare two dissimilar substances."

There is also another complication. Sodium ions are not the equivalent of potassium ions in developing solutions or in combined developer-fixer solutions. Henri Gauvin[159] compared two groups of hydroquinone developers, one containing potassium carbonate and potassium sulfite, the other containing sodium carbonate and sodium sulfite. Equivalent amounts were used in the developers. Gauvin found that the difference in the pH of the two developer compositions was not enough to explain the difference in their activities. Potassium ions seemed to have a greater response to pH changes than sodium ions in the developers. Potassium salt developers have a higher pH. The potassium salt developer has a greater capacity to neutralize the acid formed during development. A form of localized buffering maintains the potassium salt developer at a higher pH so that the developer is able to reduce more silver than a comparable sodium salt developer that operates at a lower pH and with poorer buffering.

Henri Gauvin[160] reported that the salts of sodium make developing solutions more active than the salts of lithium. Developing solutions containing mixed potassium and sodium salts were studied by Andrée Lous-Labetoulle.[161] She found that, using equal molecular proportions, a developer containing both sodium and potassium ions was more active than a solution having only sodium ions. Developing solutions made with potassium salts are more susceptible to fog formation if the developer is contaminated with sodium thiosulfate from the fixing bath. The fogging difficulty may be encountered with liquid developer concentrates, which are often compounded with potassium salts for the greater solubility of such compounds.

THE ANTIFOGGANTS

The unwanted nonimage density in a photographic layer is the result either of light or of chemical action. Chemically produced fog may have a variety of causes, but the basic mechanism is similar for the various types: silver ions from the silver halide grains are reduced to metallic silver by the donation of electrons from the developing agent. This action may occur on the surface of the grain or at a distance from it, but in either case the deposition of the silver upon the metallic silver or silver sulfide nuclei is essentially the same.

The formation of fog silver is similar to the development of the latent image. The developing agent transfers electrons to the nucleated center, in this case the fog center, giving it a negative charge. Positively charged silver

ions, either on the silver halide grain or solubilized from the grain, are attracted to the oppositely charged fog center, combining with the electrons to form metallic silver. By a repetition of this process fog silver grows until it becomes objectionable. An entire grain of silver halide may be converted to metallic fog silver. Solubilized silver ions from many grains may be deposited on suitable nucleated sites, as is the case with dichroic fog.

Latent image centers formed by the action of light and fogging centers were found to be identical by K. V. Chibisov and A. A. Mikhailova.[186] The essentials for the growth of the latent image and fog are the same: a suitable source of electrons, a nucleated center, and a supply of silver ions. Preferential destruction of fog centers would help minimize nonimage silver production, but the similarity of fog and latent image centers makes this almost impossible to accomplish. A more practical approach is to decrease the supply of silver ions by adding chemical compounds to the developer that readily combine with them. Although these compounds act upon the exposed and the unexposed grains alike, the reduction in the supply of silver ions has a relatively greater effect in restraining the formation of nonimage silver than that from latent image centers.

Fog

The developing agent, protected by sulfite and activated by an alkali, has a reducing potential that is capable of converting unexposed silver halide grains, as well as the exposed grains, to metallic silver.[162] Fog is the name given to the unwanted silver density formed in the unexposed areas of the photographic emulsion during development. Substances that favor the reduction of exposed silver halide are called developing agents, but such compounds can also be fogging agents.[163,164] The growth of fog acts to limit the degree of amplification of the latent image, as the fog may obscure important details in the areas of low exposure. The contrast of the desired image is also lowered by the veil of fog silver.

Fog is a complex phenomenon, the result of many factors related either to the photographic material or to the composition of the developer. Fog centers may be formed during manufacture of the emulsion.[165] Certain photographic films, especially those of high emulsion sensitivity, are more subject to the growth of fog than slower-speed films. Some developers, such as those of high alkalinity or high solvency for silver ions, are known to produce silver images with higher fog than developers of more moderate composition.

D. A. Veidenbakh[166] found that "hydroquinone and pyrocatechol having two negative charges, have a higher fog-forming effect on photographic materials than monoaminophenols, which carry only one negative charge

while pyrogallol, which has three charges, fogs more than the first compounds."

The total fog produced by both the emulsion and the developer was classified by M. L. Dundon and J. I. Crabtree[167,168] into these six types:

1. *Emulsion fog*, resulting from silver halide grains' becoming developable as a result of the chemical ripening process during manufacture or a continuation of the process during aging of the emulsion, or as a result of the presence of fogging impurities, or from other means that renders the unexposed grains developable.
2. *Aerial fog*, forming a developable latent image as the result of aerial oxidation of the developer in a wetted emulsion layer that is in contact with the air.
3. *Chemical development fog*, probably the result of a number of causes; it may be "a non-selective reduction, such as occurs with silver halides without the presence of gelatin," or the "reduction may be preceded by a nucleation effect which is the result of a chemical property of the developer unrelated to its reduction potential."
4. *Solvent fog*, including dichroic (two-color) fog, resulting from the deposition of metallic silver by physical development from silver ions dissolved by a developer ingredient, such as ammonia, sodium sulfite, or sodium thiocyanate.
5. *Fog from vapors and gases*, produced by contact of the emulsion layer with the vapors of certain substances, notably turpentine and resins in paints and varnishes, that form hydrogen peroxide by decomposition.
6. *Accidental light fog*, resulting from a normal developable latent image produced by unintentional and undesired exposure of the silver halide grains to actinic light at any stage during the lifetime of the photographic material.

When the accidental and secondary causes were eliminated, fog, according to T. H. James,[169] may be produced by two fundamental reactions: (1) a direct attack by the developing agent upon silver ions, either in solution or on the nuclei-free silver halide surface, or (2) as a result of the action of silver sulfide nuclei formed during the chemical ripening of the emulsion during manufacture. The direct attack upon the unnucleated surface of the silver halide should be a slow process, producing little fog silver by itself. However, this attack might produce nuclei of high activity. Such nuclei might be formed by a reduction of silver ions at the grain surface or a deposition of silver from the solution. Some silver nuclei would probably be formed in the gelatin but

not near the grain surface. The silver nuclei, either on or away from the grain surface, could then act as centers for the formation of fog.

More recently, fog formation has been shown by R. W. Swenson[170] to occur in two stages in a single emulsion layer. The first stage was called emulsion fog, a type that develops rapidly to its maximum density. The second stage—developer fog—is very slow in starting to grow, forming density slowly. Emulsion fog might be the result of excessive chemical ripening of the silver halide during manufacture or a slow continuing growth of centers where development can start reduction of a silver halide grain. This continued growth occurs during natural aging of the emulsion layer and is accelerated by high temperatures and humidities. The growth of fog centers in the emulsion during normal storage and handling is the main reason why many photographic materials have an expiration date after which use is not advised.

Aerial fog is a type of emulsion fog, formed when a developer-soaked emulsion layer is exposed to the oxygen of the air.[171] According to T. H. James,[172] aerial fog is the result of the formation of a hydrogen peroxide radical by the attack of the oxygen on the developing agent. Hydrogen peroxide is well known as a fogging agent for photographic materials.[173] Aerial fog is promoted by the presence of copper salts in the developer. Copper would exist as the cuprous form, readily reacting with oxygen to form the peroxide radical. The cuprous ion would be oxidized by this reaction to the cupric ion, but the developing agent would convert it back to the reactive cuprous state again. In this way small amounts of copper in the developer may produce a very heavy aerial fog. Copper-induced aerial fog ("tank fog") may be controlled by the addition of desensitizing dyes, such as phenosafranine, malachite green, or pinakryptol green, to the developing solution.[174] However, other investigators[175] have suggested that aerial fog in a hydroquinone developer may be caused in part by the formation of the very reactive hydroxyhydroquinone that may be formed in the alkaline developer solution.

For modern processing conditions, aerial fog and a number of other related fog-producing systems might be called oxidative fog. Such a classification would include aerial fog and all other fogs produced by intermediates of the development process. Oxidative fog would include the fog produced by aldehyde-containing hardening developers, by highly alkaline developing solutions used to force development to produce maximum emulsion speed, by Phenidone and Dimezone developers (especially if these compounds also contain fogging impurities), and by certain high-speed emulsion compositions that probably contain addenda that promote oxidative fog.

Aerial fog and some types of oxidative fog may be controlled by the presence of only two parts of some desensitizing dyes in a million parts of the developer. Phenosafranine or pinakryptol green are especially effective for this purpose. Adding sodium sulfite or potassium bromide to the developer

will also help to minimize the effects of oxidative fogging. Freshly prepared developers are more likely to exhibit aerial fog, so the use of a partially oxidized developer may be effective in controlling fog. Some developing agents after oxidation inhibit fog, apparently forming effective desensitizing dyes. Used Amidol solutions are of this type.

The emulsion fog as defined by Swenson would include any unintentional exposure to light. The latent image produced by this light would be identical to that formed by the intentional exposure. This type of emulsion fog and the latent image from the intended exposure would develop at the same rate and form the same type of silver. This silver has a high light-stopping power per quantity of silver. Obviously, it would be difficult to inhibit the formation of fog silver from the unintentional exposure of silver halide grains without also inhibiting the formation of silver from the intended latent image exposure. Sometimes mild oxidative treatments before development may destroy surface latent image but usually not without serious effect on the emulsion characteristics.

Developer fog is the formation of metallic silver by the developing agent, the slowly formed silver being of a type that has low light-stopping power. This low density of silver remains low, even during extended development, and does not approach the density of a like amount of silver produced by the development of emulsion fog. Increasing the pH of the developer—that is, increasing the activity of the developing agent—and the presence of certain dyes and emulsion addenda also increase the formation of developer fog. According to Swenson, "Developer fog neither starts nor continues on a grain but is external to the grain; otherwise, the silver formed by the reaction might be expected to behave similarly to a latent image and start a 'catalyzed' reaction."

Dichroic Fog

Dichroic fog is one form of developer fog that may be encountered by almost every processor of photographic film. It is also one of the easiest forms of fog to identify. This two-color fog is composed of metallic silver, usually on the surface of the emulsion. The color depends on how a negative is viewed; by transmitted light, the color is red to orange-red; by reflected light, the color is yellowish green, often having a silvery, metallic hue. The exact color depends upon the size of the silver particles, so that the range of colors may be considerable. By reflected light a film negative may appear opaque, giving the appearance of incomplete fixation.[176]

Dichroic fog is very easily produced on modern high-speed photographic films when these are processed in developers containing silver solvents, such as thiocyanate salts. Apparently, certain speed-increasing emulsion addenda

provide or are instrumental in forming nucleation centers for the formation of a scum of metallic silver on the emulsion surface. Manufacturers of photographic film often warn against the use of solvent developers for processing such films.

Dichroic fog is not a new problem, however. In 1903 it was thoroughly investigated by A. and L. Lumière and A. Seyewetz.[177] Dichroic fog may be produced by a deposition of metallic silver from a developer containing solubilized silver ions, or the metallic silver may be deposited in a nonacidic or exhausted acidic fixing bath having a high concentration of dissolved silver. In either case the metallic silver results from the action of the developing agent upon the solubilized silver in the processing solution. Solvents of silver halide, such as sodium thiosulfate, potassium thiocyanate, and ammonia, promote dichroic fog formation. Underexposed photographic materials are more prone to fogging than fully exposed ones because more undeveloped silver halide is available for dissolution. Prolonged development, high-temperature development, or highly accelerated development promote the solubilization and deposition of silver on the surface of the emulsion. The introduction of an emulsion layer containing a very active developer into a well-used, weakly acidic fixing bath represents ideal conditions for the precipitation of a metallic silver layer on the emulsion surface. The Lumières and Seyewetz[178] suggested neutralized potassium permanganate followed by a sodium sulfite bath as the best means to remove dichroic fog. A bath containing sodium thiosulfate and citric acid was also effective.

Dichroic fog requires nuclei on the surface of the emulsion or in the gelatin before objectional deposition of metallic silver scums can be obtained. Development stain (dichroic fog) is related to presence of sodium sulfite in the developer.[179,180] One active form of nuclei in the developer may be sodium sulfide, formed by certain fungi and bacteria in the developing solution that are able to reduce sodium sulfite, sodium sulfate, or sodium thiosulfate to sodium sulfide.[181,182] R. W. Henn and J. I. Crabtree[183] state that as little as one part of silver sulfide per one million parts of developer is sufficient to produce a surface stain, and concentrations of 50 ppm or more will produce black fog. Silver formed by physical development is deposited around the silver sulfide nuclei.

Dichroic fog resulting from the precipitation of metallic silver upon sulfide nuclei may be controlled by forming a sulfide compound that has low solubility in the developer. Lead nitrate or acetate, or cadmium chloride, is effective in minimizing the effect of sulfide nuclei in the solution. A very dilute solution of cadmium chloride, 0.25 to 0.5 g/liter of developer, was found to be the most effective.

Once formed, the finely divided silver stain may be difficult to remove completely. The finely dispersed silver may be solubilized with a minimum

amount of attack on the coarser image silver by the use of a weak reducing solution. An acid solution of ammonium thiosulfate, especially a rapid liquid fixer with a hardener, is an excellent slow-acting silver remover when 15 to 30 g of citric acid are added to a liter of the working solution of the fixing bath. The hardening ammonium thiosulfate fixing bath may be used without the citric acid, but the temperature of the bath should be raised to 100°F to accelerate its action. All film should be well washed after the silver stain has been removed.[184,185]

Inorganic Antifoggants

Inorganic compounds that inhibit fog, such as potassium bromide, which was used first in 1863 by C. Russell,[187] are called restrainers. M. Carey Lea[188] found potassium iodide to be more effective than bromides or chlorides in a ferrous sulfate-sodium tartrate developer. The developer composition plays a role. Low-pH Metol-hydroquinone developers are adversely affected by the presence of bromide in the developer solution. But, according to A. J. Axford and J. D. Kendall,[189] "Similar increases in the soluble bromide concentration of low pH developers based on Phenidone/hydroquinone have comparatively little effect." More effective organic compounds were called antifoggants. However, the action of both types of compounds is essentially the same so all fog-inhibiting compounds might well be referred to simply as antifoggants.

According to C. E. Kenneth Mees,[190] "The solubility of silver bromide in dilute potassium bromide solutions is so low that the point of minimum solubility is difficult to measure." The solubility of silver bromide in the potassium bromide reaches its minimum at about 0.001 of the molecular weight of potassium bromide in a liter of solution. The soluble bromide ions of the solution combine with silver ions on the grain surface, forming insoluble silver bromide. Fewer silver ions are available for the building of fog centers, and potassium bromide thus acts to restrain the development of nonimage silver. The bromide ions from the developer may also be adsorbed to the surface of the grain. This would produce a negatively charged barrier around the grain that would inhibit the access of negatively charged developing agents to the grain surface. The net effect of soluble bromide in the developer is to delay the formation of fog until the development of the latent image has reached its desired stage. Bromide may also restrain the development of the latent image, reducing both the contrast and density produced, but the effect is greater upon the nonimage silver development.

Once the minimum point of solubility of silver bromide in potassium bromide solutions is passed, the silver bromide becomes more soluble because of the formation of complex ions of silver and bromide. High

concentrations of potassium bromide, and potassium iodide as well, have such a great solubilizing effect on silver bromide that such concentrated solutions may be used to dissolve rapidly all the unused silver bromide in the emulsion layer. The color of developed silver may become warmer in tone when a considerable quantity of potassium bromide is present in the developer. (See Figure 3.)

At low concentrations potassium iodide is also an effective fog restrainer. For shorter times of development A. P. H. Trivelli and E. C. Jensen[200] found the fog-removing power of potassium bromide to be greater than that of potassium iodide, but for longer times of development potassium iodide had the greater fog-suppressing power. Potassium iodide forms the very insoluble silver iodide when the potassium iodide reacts with silver ions. In practice the quantities of potassium iodide added to the developer are less than those of potassium bromide. Quantities of potassium iodide greater than 0.1% are

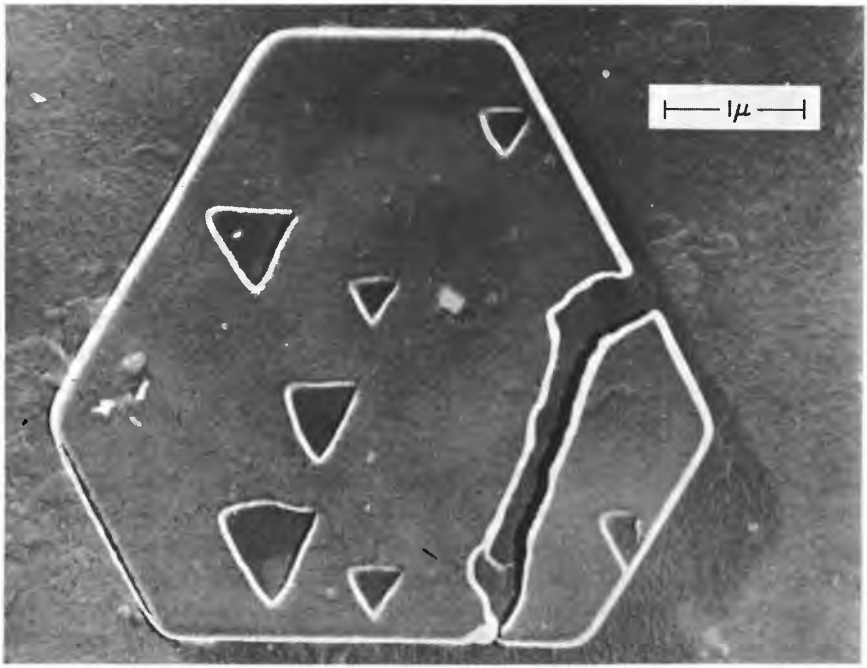


Figure 3. Electron micrograph of a silver bromide grain etched in 10% potassium bromide for 30 sec. The micrograph shows isolated pits as well as a trough formed by preferential etching at a strained region of the grain. This grain was apparently deformed over the edge of an underlying grain by the compressive force of the drying gelatin. [J. F. Hamilton, L. E. Brady, and F. A. Hamm, *J. App. Phys.*, 29: 800 (1958)]

rarely used because of the great retardation of development and the difficulty in fixing out the silver iodide that is formed.

If both potassium iodide and potassium bromide are present in the developer, the restraining action is at first due primarily to the iodide. When the iodide is used up, then the bromide is the restrainer. In this way developers may be compounded that exhibit equal restraint as the developing agents undergo exhaustion. Sodium or potassium chloride shows some restraining action, especially with chloride emulsion layers, but soluble chloride is little used commercially. Under certain conditions H. D. Murray and D. A. Spencer[191] found sodium thiosulfate to be more effective in repressing fog than a soluble bromide.

Organic Antifoggants

Organic compounds when added to the developer may also affect fog formation. The reaction of the organic compound with silver ions on the surface of the grain may produce a silver compound that may be more soluble, less soluble, or equal to the solubility of silver bromide, the main silver salt in many photographic materials. G. P. Faerman[192] reported than when the silver salt formed with the organic compound was more soluble than silver bromide, the silver of the salt was more susceptible to reduction than silver bromide and hence more likely to promote fog formation. Little effect was noticed when the silver salt with the organic compound had a solubility similar to that of silver bromide. However, when the silver salt of the organic compound was less soluble than silver bromide, the reduction of the silver was decreased, that is, the organic compound was an antifoggant.

The solubility of the silver salts of some organic antifoggants is extremely low. These substances would be adsorbed to the grain surface strongly. Bromide ions on the grain surface would be displaced by the organic molecules. At sufficient concentrations the entire grain surface may be coated with a layer of a silver salt of very low solubility. R. J. Newmiller and R. B. Pontius[193] found that the clean surface of metallic silver was covered with a monomolecular layer of either potassium iodide or 1-phenyl-5-mercaptotetrazole but that benzotriazole did not cover more than 15% of the silver surface. The 1-phenyl-5-mercaptotetrazole completely stopped the physical development process when it was present in a concentration equal to a monomolecular layer, but the effect of benzotriazole under similar conditions was insignificant.

Most organic antifoggants are weak acids. The ionization of these acids would be effected by the alkalinity of the developer solution. G. P. Faerman[192] found that the rate of reduction of the silver salts of organic antifoggants varied with the solution pH. The order of effectiveness of a number of

Table 3. Order of Decreasing Solubility of Silver Salts

pH = 6.5	pH = 10.6
2-Methylbenzimidazole	5-Methyl-7-hydroxy-1,3,4-triazaindolizine
Benzimidazole	Benzimidazole
5-Nitrobenzimidazole	2-Methylbenzimidazole
5-Methyl-7-hydroxy-1,3,4-triazaindolizine	Silver bromide
Benzotriazole	5-Nitrobenzimidazole
Silver bromide	Benzotriazole
1-Phenyl-5-mercapto-tetrazole	1-Phenyl-5-mercapto-tetrazole

antifoggants may change with pH in the same way that the solubility of the silver salts of the antifoggants changes with pH. (See Table 3.)

At pH = 6.5 only the silver salt of 1-phenyl-5-mercaptotetrazole is less soluble and more difficult to reduce than silver bromide. But at pH = 10.6 the silver salts of benzotriazole and 5-nitrobenzimidazole were also less reducible than the silver bromide and were thus effective antifoggants at that pH. At pH = 10.6 the silver benzotriazolate at 25°C is five times less soluble than silver bromide; at pH = 4.6 silver benzotriazolate is 10 times greater in solubility than silver bromide. At pH = 4.6 benzotriazole has no antifoggant action, but in a developer solution of pH = 10.6 the benzotriazole would combine with silver ions. A silver benzotriazolate would be attached to the grain surface, displacing bromide ions. The rate of image development would be slowed, but the restraint would be greater in effect in the areas of very low or no exposure. Benzotriazole at pH = 10.6 is an antifoggant. The extent of the antifogging action would depend on the concentration of the benzotriazole, as the quantity would help to determine the extent of the surface coverage.

The use of organic antifoggants arose from the study of the action of organic compounds, usually containing sulfur, contained in gelatin upon the sensitivity of silver halide emulsions. S. E. Sheppard,[194–198] from his study of gelatin impurities, proposed that antifogging substances such as thioacetamide formed a silver compound at the interface between the sensitizing specks of silver sulfide and the highly reactive silver bromide surrounding the speck on the surface of the silver halide. The low solubility of the salt formed by the silver ions and the antifoggant would insulate the sensitivity specks that had served as the site of the latent image formed by

light exposure. The insulating effect would be the most effective with sensitivity specks that were not the site of latent image formation.

The earliest organic antifoggants were derived from those compounds found to be effective in inhibiting the growth of fog in photographic emulsions because of the continued chemical ripening of the emulsion. Peter Wulff and Bruno Wendt[199] patented imidazole compounds for inclusion in emulsions to overcome the fog produced by active gelatins. A. P. H. Trivelli and E. C. Jensen[200] found that one of the patented compounds, 6-nitrobenzimidazole, was superior to potassium bromide as an antifoggant in developers. This organic compound caused less loss of image density without changing the emulsion speed produced by a *p*-aminophenol developer. The sodium salt of 6-nitrobenzimidazole was claimed to be superior in properties.[201] Two sulfur-containing compounds, cysteine hydrochloride and thiobarbituric acid, were later reported by these investigators[202] to be effective antifoggants but with greater image density loss than that given by 6-nitrobenzimidazole. Thiosalicyclic acid at a concentration of 0.01 to 1.0 g/liter of developer was patented by Harold D. Russell[203] as an antifoggant. Cysteine derivatives have also been patented.[204]

Many thousands of organic compounds, usually containing sulfur or nitrogen in a ring or with a mercapto (—SH) group, or both, have been found to influence the development of fog and image density.[205–212] Such compounds have been used in the developers for negative, reversal, or color processing. Control of fog is essential with reversal color processing, so that satisfactory dye saturation is achieved in the positive color transparency. Antifoggants are also used to suppress fog formation in outdated photographic papers.

Significant Compounds in Practice

Despite the great number of compounds studied as antifoggants, and despite the wide variety of uses, the number of antifoggants actually used in practice remains quite low. The most important ones contained in developers today include

- potassium or sodium bromide
- potassium or sodium iodide
- benzotriazole
- 5-methylbenzotriazole
- 6-nitrobenzimidazole
- 1-phenyl-5-mercaptotetrazole
- 2-benzoxazolethiol
- 2-benzimidazolethiol
- sodium anthroquinone sulfonate.

The exact amount of an antifoggant to be added to a developer is the minimum amount to suppress fog without causing unacceptable loss of emulsion speed and image density. This quantity depends on so many factors that usually it has to be determined empirically. The quantity for equal fog control will vary with the nature of each antifoggant. The developing agents and other ingredients of the developer are also a factor, as are the time and temperature of development. The type of photographic emulsion and its age will also influence the choice and quantity of an antifoggant for a developer. For a working solution of a negative developer L. F. A. Mason[213] suggests that potassium bromide may be used from 1 to 15 g/liter of developer but that potassium iodide should only be present in amounts of about one thousandth of the bromide. A useful concentration of benzotriazole is about 0.2 g/liter of the developer, but 1-phenyl-5-mercaptotetrazole is much more effective, requiring only 0.02 g/liter of developer for negative materials.

In practice antifoggants are used for a wide variety of purposes. Most of the organic compounds cause the developed image to be colder in tone—that is, more bluish—than the image produced by a developer without the antifoggant.[214] 5-Aminobenzotriazole is such a compound.[215] Excess antifoggant in a developer may be added to minimize the effect of known overexposure, although the image may need to be intensified as part of the treatment. The antifoggant may be removed from a developer in case of known underexposure, but important details in the areas of low exposure may be obscured by the fog level.

Probably one of the most useful effects of an antifoggant in a complete developer is the suppressing of age fog on photographic paper, thus saving it for making prints. A table was devised by Joseph A. Schantz[216] for the addition of either a 0.2% benzotriazole solution or a 0.5% 6-nitrobenzimidazole nitrate solution to a conventional Metol-hydroquinone developer to be used at 68°F. Table 4 includes not only outdated papers but also black-and-white and color reversal films.

A multitude of compounds can function as antifoggants, and their mechanism is essentially the same. This mechanism has been worked out largely by studies on 1-phenyl-5-mercaptotetrazole and various benzotriazoles.[217–221] When the antifoggant is introduced into a photographic emulsion, it forms a compound with silver ions that is difficultly soluble. This compound forms on the surface of the silver halide crystals, increasing the difficulty of developing the unexposed grains more than that of the exposed grains.[222] Some of the silver compounds with the antifoggant may actually destroy latent images, particularly the small fog images or images in the area of weak exposure.[223] The antifoggant may adsorb to the metallic silver of the latent image, interfering with the electron transfer from the developing agent to the metallic silver. An antifoggant such as 1-phenyl-5-mercaptotetrazole is

Table 4. Addition of Antifoggant to Developer

Material	Fog Condition	0.2% Benzotriazole: Add per Liter	0.5% 6-Nitro benzimidazole nitrate: Add per Liter
Outdated papers	Light	50 ml	10 ml
	Medium	150 ml	20 ml
	Heavy	300 ml	60 ml
	Very heavy	500 ml	100 ml
Black-and-white films	Light	20 ml	10 ml
	Heavy	40 ml	20 ml
Reversal color films	Light to medium	25 ml (added to the first developer)	6 ml

known to adsorb to metallic silver, but an antifoggant such as benzotriazole does not adsorb strongly enough to affect the electron transfer rate as much.

WATER

Water is virtually the universal solvent for the making of photographic solutions. It provides an almost ideal medium for the dispersal and ionization of the developing and other chemicals needed to produce the photographic image, in either metallic silver or colored dyes. Unfortunately, water also provides the same medium to any salts or gases that may contact it before it is put to photographic use. Because water may represent over 80% of all the chemicals in a photographic solution, dissolved or suspended impurities may be sufficient to cause undesirable photographic effects.

The water derived from rivers, lakes, springs, or wells may contain a wide variety of impurities, of which the more important may be classified as follows:

1. Dissolved salts such as the bicarbonates, chlorides, and sulfates, chiefly of calcium, magnesium, sodium and potassium, but also to a lesser extent of aluminum, iron, manganese, and zinc.
2. Suspended matter, such as mud, silica, iron rust, free sulfur, or organic matter, often in so small a particulate state as to pass through fine-pore filters.
3. Dissolved gases, such as air (oxygen and nitrogen), carbon dioxide, ammonia, and chlorine, or sulfurous gases, such as sulfur dioxide or hydrogen sulfide.

4. Other diverse impurities, as trace metals, either dispersed or as salts of copper, iron, lead and tin; organic growths, such as algae, slimes, molds, and bacteria; insoluble material of a wide variety; and various impurities that are just termed pollution, usually the result of man's unconcern.

Hardness

Water's hardness is a result of the presence of calcium and magnesium ions in dissolved salts. Salts of aluminum, iron, manganese, and zinc also may cause hardness in water, but usually they are not present in sufficient quantity to cause appreciable hardness. Water hardness is measured by a method that does not distinguish between any of the constitutents but reports them as parts per million of calcium carbonate. Sometimes water is classed in degrees of hardness; for example, one degree may represent 10 ppm of calcium carbonate. At present there is no common international standard of hardness, but the following classification has been suggested by Lloyd E. West:[224]

Description of Hardness	Hardness (as $CaCO_3$ in ppm)
Very hard	Over 200
Hard	120–120
Moderately hard	40–120
Soft	Less than 40

Water's hardness is a characteristic of its source and varies widely throughout the world. Even within a city the hardness may vary if water is derived from more than one source.

Although water hardness may be the result of many compounds, those of calcium and magnesium are the major cause. In most fresh water there is about four times as much calcium as magnesium, and most of the hardness is usually in the form of bicarbonate salts. When rain falls on chalky soil, carbon dioxide from the air forms an acid solution in the rain water which dissolves some of the calcium salts of the soil or rock as follows:

$$H_2O + CO_2 + CaCO_3 \longrightarrow Ca(HCO_3)_2$$

The calcium bicarbonate formed is soluble in the water. Rain water containing carbon dioxide that contacts magnesium carbonate will form water-soluble bicarbonates of magnesium.

All water from natural ground sources contains hardness due to dissolved salts. When hard water is used to prepare alkaline developers, there is an interaction between the bicarbonate salts and the alkali.

$$Ca(HCO_3)_2 + 2NaOH \longrightarrow CaCO_3\downarrow + Na_2CO_3 + 2H_2O$$

One result of the reaction of calcium bicarbonate and sodium hydroxide is to produce insoluble calcium carbonate, here designated by a downward-pointed arrow to indicate that this compound would be precipitated from the alkaline developer solution. Only 12 to 14 ppm of this white compound are soluble in water. Another result is to use up some of the alkali of the developer.

If sodium sulfite is present in a developer made with hard water, fine needle-shaped crystals of calcium sulfite will settle from the solution and sometimes may adhere to the emulsion side of the photographic material. Only about 43 ppm of this white compound are soluble in water at 65°F. The calcium sulfite is formed by the following reaction:

$$Ca(HCO_3)_2 + Na_2SO_3 \longrightarrow CaSO_3\downarrow + 2NaHCO_3$$

A developer made with hard water loses some of its alkali and sulfite to form the insoluble calcium salts that precipitate from solution. According to J. I. Crabtree and G. E. Matthews,[225] this loss is negligible, except in the case of developers of low alkalinity, such as those containing a low concentration of borax as the alkali. If the white precipitate or sludge formed from the hard water of a developer is allowed to settle and only the clear solution is used, there is little harm in using hard water containing bicarbonates to make developing solutions. Magnesium salts are usually not precipitated unless there is an excess of these ions in the water. Magnesium sulfite is relatively soluble (1250 ppm) but magnesium carbonate is less so.

Calcium or magnesium bicarbonates may be decomposed by boiling the water.

$$Ca(HCO_3)_2 + \text{heat} \longrightarrow CaCO_3\downarrow + CO_2 + H_2O$$

Calcium carbonate is precipitated; often it may be seen as a hard scale lining the vessel used to contain the boiling water, as occurs inside a boiler, tea-kettle, water lines, or processing tanks. Because hardness due to bicarbonate salts may be removed so easily, this type of hardness is said to be "temporary."

Calcium and magnesium may also be present in hard water as chlorides or sulfates. Because the compounds are not decomposed when the water is boiled, this hardness is said to be "permanent." Calcium sulfate will react in an alkaline developer to produce calcium carbonate by the following reaction.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$

Calcium sulfite may also be formed.

$$CaSO_4 + Na_2SO_3 \longrightarrow CaSO_3\downarrow + Na_2SO_4$$

Such reactions occur slowly and the precipitated calcium salts do little harm, as in the case of those salts formed by the temporary hardness of water,

if not allowed to be present in the developer during use. J. I. Crabtree and G. E. Matthews have found that calcium and magnesium salts, both chlorides and sulfates, need to be present in a concentration greater than 0.1% to exert an appreciable effect on a developer containing 0.3% sodium carbonate. In the United States the maximum permanent hardness of natural water was found to be only 0.04% calculated as calcium carbonate. The loss of alkali or sulfite from a developer made with hard water would not appear to be significant if made with natural water of even the maximum permanent hardness in this country.

Methods of Minimizing Water Hardness

Difficulties due to either temporary or permanent hardness of water are primarily the result of the precipitation during processing of the insoluble calcium salts: calcium carbonate, calcium sulfite, calcium phosphate, calcium borate, and others. The remedy is to remove the calcium from the water used in the processing solutions. Removal of the calcium may be accomplished in several ways. One chemical method involves combining the calcium ion into a more complex but water-soluble ion that does not precipitate. Effectively, the calcium ion is no longer free to react with the alkali or the sulfite of the developer. The calcium ion is said to have been "sequestered" (from *sequester*, the Latin word meaning to place in safe keeping). Photographic sequestering agents may be either organic or inorganic in nature. Even though the natural water used for making photographic solutions may be relatively free of calcium and magnesium salts, sequestering agents are needed because the gelatin of photographic products often contains a considerable amount of calcium ions.

Inorganic Sequestering Agents

Among the first sequestering agents were the polyphosphates: sodium tetraphosphate, $Na_6P_4O_{13}$ (sold under the trade name Quadrafos); sodium tripolyphosphate, $Na_5P_3O_{10}$; sodium trimetaphosphate, $Na_3P_3O_9$; and polymeric forms of sodium hexametaphosphate having the general formula $(NaPO_3)_n$, where n is six or greater. The polymeric form of sodium hexametaphosphate is sold under the trade name Calgon, but care must be taken that the commercial product contains only sodium hexametaphosphate.

These complex phosphates serve as sequestering agents for calcium and magnesium ions in alkaline developers, providing the developer has not been made with an orthophosphate as a source of alkali. Quantities of about 0.5

to 2.0 g of the phosphate per liter of developer are useful to reduce sludging due to water hardness, but doubling the quantity of the sequestering agent does not sequester exactly twice the quantity of the calcium or magnesium ions. R. W. Henn and J. I. Crabtree[226] state that 0.5 g of sodium tetraphosphate is sufficient for low- or medium-pH developers, but 2 g/liter is needed for higher-pH carbonate developers. The efficiency of the phosphates in removing calcium or magnesium ions depends upon the solution alkalinity in the pH range from 9.0 to 10.5. The sequestering action becomes less effective as the pH rises.

Polyphosphates react slowly with water in an alkaline developer solution forming simple orthophosphates. Sodium tripolyphosphate, for example, undergoes the following reaction.

$$Na_5P_3O_{10} + H_2O \longrightarrow Na_3HP_2O_7 + Na_2HPO_4$$

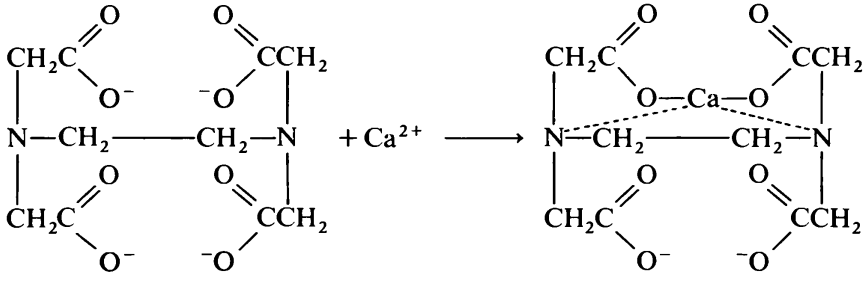
Any calcium ions that might have been held by the tripolyphosphate are released and immediately form an insoluble precipitate of calcium phosphate. Insoluble calcium carbonate may also be formed. The insoluble calcium salts resulting from the hydrolysis of the phosphate may coat the equipment or photographic material during processing. The pH of the developer may be lowered by the hydrolysis that produces sodium dihydrogen phosphate, and this may result in some loss of developer activity. Disodium hydrogen phosphate is alkaline; the hydrolysis of sodium tetraphosphate yields both acidic and alkaline phosphates, producing little change in developer activity.

Phosphate sequestering agents should not be used in concentrated stock solutions of developers that are to be stored for some time before use. According to L. F. A. Mason,[227] the hydrolysis of phosphates may occur even in dry mixed powders that are stored. Calgon is said to be the best sequestering agent of the phosphates, but its use is limited by its tendency to take up water, becoming sticky and hydrolyzing. Calgon therefore should not be kept in contact with the sulfite or the alkali of a developer for any length of time before the solution is mixed.

The tripolyphosphate does not take up water from humid air and is often used in mixtures of the powders of the ingredients of a developer, or it may be combined with Calgon to minimize the hydroscopic nature of the Calgon. Organic hydroxy acids or their salts, such as citric acid or sodium citrate, tartaric acid, and others, are often used to minimize the hydrolysis of the phosphate. Disodium citrate at about two to four times the weight of the tetraphosphate is said to double the life of the tetraphosphate's sequestering action and to prevent the aluminum phosphate scum that forms in the fixing bath when the tetraphosphate does hydrolyze. If calcium or aluminum scums do form, they may be removed by immersion in 5% acetic acid solution. An aluminum sulfite scum is solubilized by a treatment with 2% sodium hydroxide, but this solution will not remove calcium scums or scales.

Organic Sequestering Agents

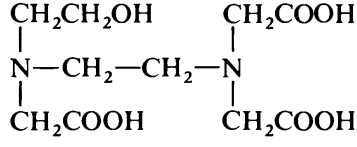
Many organic compounds act as sequestering agents, but those most used in photography are usually nitrogen-containing acids. These compounds holds calcium and metal ions by a combination of salt formation and the attractive forces of the nitrogen atoms. Probably the most used compound is ethylenediaminetetraacetic acid (called E-D-T-A and written EDTA), which sequesters calcium ions in alkaline solution by the following method:



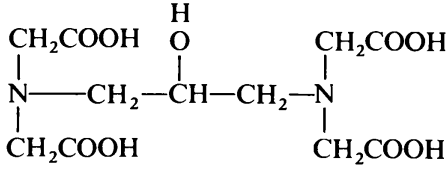
ethylenediaminetetra-acetic acid (ionized)

sequestered calcium held by ethylenediaminetetra-acetic acid

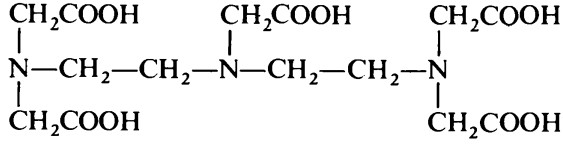
EDTA is sold under a number of trade names, one being Sequestrene. The disodium salt is called Sequestrene Na2, the trisodium salt is called Sequestrene Na3, and the tetrasodium salt is known as Sequestrene Na4. A considerable variety of compounds are commercially available that are related to EDTA in some degree, such as the following:



hydroxyethylethylenediaminetriacetic acid



1,3-diamino-2-propanol-tetraacetic acid



diethylenetriaminepentaacetic acid (DTPA)

Only small quantities of the organic sequestering agents are needed—about 2 g/liter of developer. But if ferric ions are present in the developer, the presence of EDTA enhances the oxidation of the developing agent by reaction with the air. Paul M. Mader[228] proposed that EDTA forms a complex ion with ferric ions in the solution, this complex ion serving to promote "the otherwise unimportant reaction between the developing agent and hydrogen peroxide. This hydrogen peroxide is a product of the reaction between the developing agent and oxygen. The increase in the rate of loss of developing agent caused by addition of EDTA to the solution is due to catalysis of both the hydrogen peroxide–developing agent and oxygen–developing agent reactions by the EDTA–ferric iron complex."

Organic sequestering agents of the EDTA type form complexes with calcium and magnesium that become less stable as the temperature of the processing solution rises. This instability has been reported to be just apparent at 80°F and becomes increasingly so as the temperature rises.

As do most organic amines, the EDTA-type compounds act as silver solvents, promoting physical development and the possibility of dichroic fog. In his book L. F. A. Mason[227] reported the work of R. E. Moore, who found that 1 g of each of the following three compounds in 100 ml of alkaline solution dissolved silver bromide to the extent listed.

Compound	Silver Solubilized
Ethylenediaminetetraacetic acid	0.013 g
Diethylenetriaminepentaacetic acid	0.019 g
Triethylenetetraminehexaacetic acid	0.037 g

Removal of Calcium and Magnesium Ions from Water

Calcium ions, the primary cause of scums and scales, may be removed from hard water before use by precipitation as an insoluble salt. Calcium oxalate is a compound of even less solubility than the difficultly soluble calcium carbonate, only 0.0059 g of calcium oxalate being soluble in 100 ml water at 18°C. Adding a solution of sodium oxalate to hard water will precipitate calcium oxalate. The sodium oxalate is added until no further precipitate is formed. Then, after the precipitate has settled, the water is decanted and ready for use. J. I. Crabtree[229] found that even the presence of 1% sodium oxalate in the water had no effect on the developer activity.

Boiling water and condensing the steam is the way distilled water is made. The salts dissolved in the natural water are left behind when the steam escapes. Distilled water is free of the salts of temporary or permanent hardness, making this purified water ideal for mixing photographic solutions,

especially developers. Care should be taken that impurities are not introduced into distilled water from the containers, piping, or other vessels that may contact the water.

Calcium and magnesium ions may be removed from hard water by passing the water over complex sodium aluminum silicates (zeolites).[230] The complex silicate exchanges its sodium ions for the calcium and magnesium ions in the water.

sodium aluminum silicate (zeolite) + calcium sulfate ⟶
calcium aluminum silicate + sodium sulfate

The calcium aluminum silicate is insoluble in water but the sodium sulfate is dissolved in the water. After use, the zeolite becomes saturated with the calcium and magnesium ions removed from the hard water. These ions are flushed from the zeolite by treating it with about a 12% solution of sodium chloride, which regenerates the zeolite for further water treatment.

calcium aluminum silicate + sodium chloride ⟶
sodium aluminum silicate + calcium chloride

The hardness of natural water is removed by converting the calcium and magnesium salts of the hard water to sodium salts by contact with a bed of sodium aluminum silicate. The calcium or magnesium ions held by the complex silicates are then displaced by using a strong solution of sodium chloride, regenerating the complex silicates for further water treatment. This procedure may be repeated a number of times to free the hardness from water. In practice, however, some hardness may be allowed to remain in the water so as to extend the periods before the regeneration is needed. It should be noted that the temporary hardness of water is converted to sodium bicarbonate. If water containing this compound is heated, carbon dioxide gas is expelled, forming sodium carbonate, a compound that raises the pH of water and may make the water unsuitable for certain photographic uses.

Water may be freed of its dissolved salts by passing the water over ion-exchange resins.[231] These resins are polymeric compounds, such as the sulfonated polystyrene sold under such commercial names as Dowex-50, Amberlite IR-120, Permutit Q, and others. This copolymer of about 90% styrene and 10% divinylbenzene is formed in small round beads, which are then treated with strong acid to form about one sulfonic acid group on each monomer of the polymer. Polyvalent ions are taken up preferentially over monovalent ions. From dilute solutions such as natural water, the calcium and magnesium ions are largely removed, because the sulfonates of these ions are much less soluble than the sulfonates of sodium or potassium.

One resin bed may contain a cationic exchange resin, such as the acidic sulfonic acid resin described; a second bed may contain an anionic resin in a

basic state, such as a quaternary ammonium resin.[232] The acidic cation resin bed removes the ions of calcium, magnesium, sodium, potassium, and so on, but the acidic radicals of these salts are still present in the water. These dilute acids are then adsorbed by the alkaline resins of the second bed, giving demineralized water suitable for photographic purposes. Both beds may be regenerated repeatedly for further use by treating the cationic resin with acid and the anionic resin with caustic solution.

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Chapter 6
The Mechanism of Development

What the actual nature of the reduction centre is, and how it is rendered active by the action of light and of chemical reducers, remains to be seen.

WALTER CLARK[93]

Only limited information concerning the mechanism of development can be obtained by direct observation. W. Scheffer[1] used the light microscope to observe the first traces of the effect of development upon silver bromide crystals. Fine silver filaments were found to protrude from the surface of the crystal "something like that of a hedgehog with comparatively few spines."[2] In 1917 Millard B. Hodgson[3] also used high-power microscopic magnification to examine silver halide grains at various stages of development. He reported that "In most cases, development starts at considerably more than one particular point, even in the case of small fragments, and continues (provided time is allowed) until the entire crystal is reduced." Photomicrographs made by A. P. H. Trivelli[4,5] indicated an apparent relationship between the chemical activity of the developer and the distortion of the crystal form that occurred upon development. With hydroquinone development, most of the crystals retained their original shape after being reduced to

metallic silver; Metol and other developing agents of greater activity caused greater and greater distortion of the crystal shape. Others[6] have also used light microscopes to study the metallic silver produced by various developing agents. (See Figure 1.)

Motion pictures of the development of a photographic image were taken through a microscope by Clifton Tuttle and A. P. H. Trivelli.[7] Development by Elon started from centers on the grain, the grain being in constant vibration, throwing out "thread-like protuberances which likewise are in rapid movement." Developing agents of high activity showed violent action, often destroying the exterior outline of the grain. Compounds of lower potential, such as hydroquinone, caused less change in the grain outline. H. Frieser[8] has also studied the chemical and physical development of silver halide crystals. Development of very coarse-grained silver halide crystals was observed by motion pictures by Shin Fujisawa, Eiichi Mizuki, and Kikuo Kubotera.[9]

The ability of a light microscope to resolve fine details of an object is limited by the degree of perfection of the lens system and by the wavelength of the light on the object.[10] According to Edwin E. Jelley,[11]

> The theoretical limit to its resolving power, using violet light with an apochromatic objective of 1.40 N.A., is 0.16 μ (1/159,000 inch). In actual photomicrographic practice, the limit is nearer 0.20 μ (1/127,000 inch) as lens flare becomes a serious factor when photomicrographing very small silver granules with the full aperture of the objective. At these high apertures, the depth of focus is approximately 0.2 μ, or roughly the same as the resolution. This limits the region of focus to a plane, so that what is termed an "optical section" of the object is seen; and this is complicated by shadows cast by its out-of-focus parts. In order to gain a mental picture of what this ratio of resolving power to depth of focus really means, let us suppose that your eyes had a depth of focus equal to their resolution: you would then have great difficulty in reading the time on your watch, for when the eye was focused on the hour hand, both the minute hand and the numerals would be so far out of focus as to be invisible! In examining a minute object with the highest powers of the optical microscope, it is necessary, therefore, to study all its "optical sections" in order to arrive at a three-dimensional interpretation. In addition, the interpretation of the microscope image of very small objects (below about 2 μ in diameter) is complicated by the fact that a microscope objective with a numerical aperture of 1.40 collects all the light rays from an object within a cone of 136°, so that at least five faces of a cube are seen at once; and all six are visible when the cube stands on a corner.

Electrons may be considered to have a wavelength that depends upon their velocity. A beam of electrons accelerated by 60,000 V behaves as though it had a wavelength of 0.05 Å, which is about 1/80,000 of the wavelength of violet light. A resolution of 50 Å is obtained when the numerical aperture of the electron microscope is 0.0015. The depth of focus with such a small angle of

Figure 1. (*a*) **At an early stage of development, silver particles form at particular sites on the silver halide grain, but if development is continued,** (*b*) **the entire grain is reduced to metallic silver. Crystal form may be largely preserved if a low-solvent, "distortionless" hydroquinone solution is used as the developer. (John F. Hamilton, Eastman Kodak Company)**

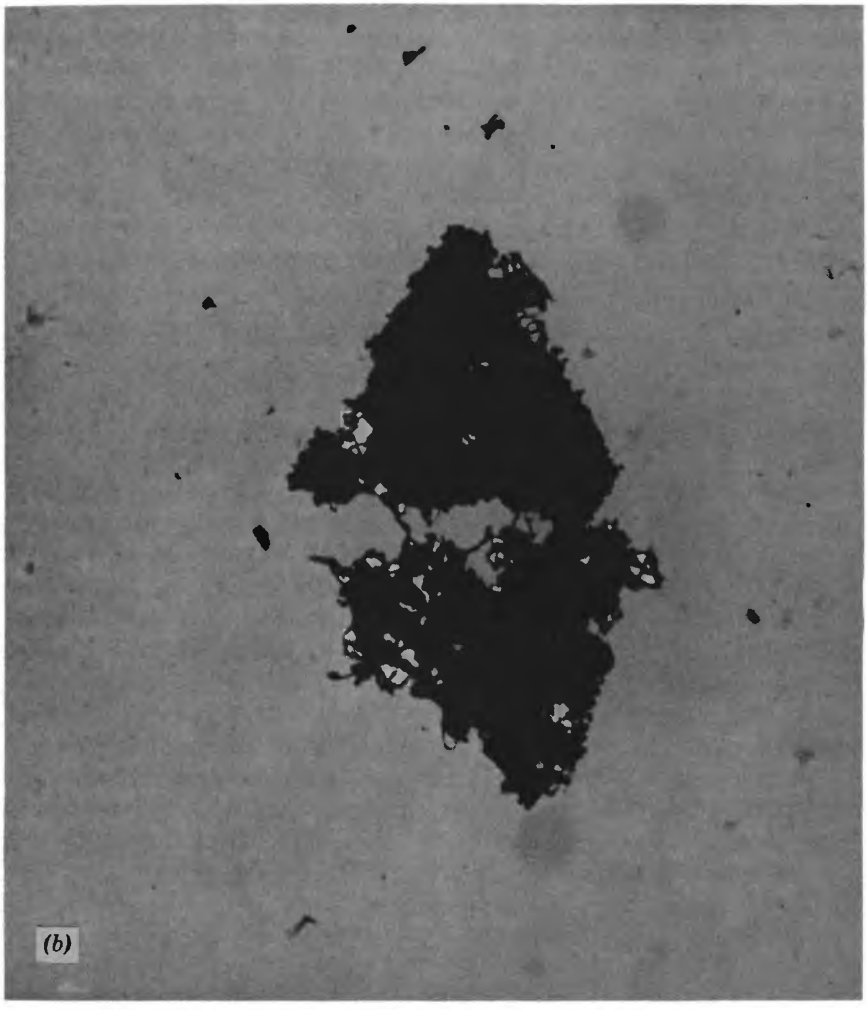


Figure 1. (*continued*)

illumination is about 2 μ, so that small particles appear in about the same perspective as visible objects appear to the human eye. Continued improvement in electron microscope construction has made this instrument even more effective, using accelerating voltages of 100,000 V to produce an electron optical magnification of 150,000 times.

Electron microscopy was immediately adopted as a routine tool for studying the development of photographic materials. (See Figure 2.) In 1940

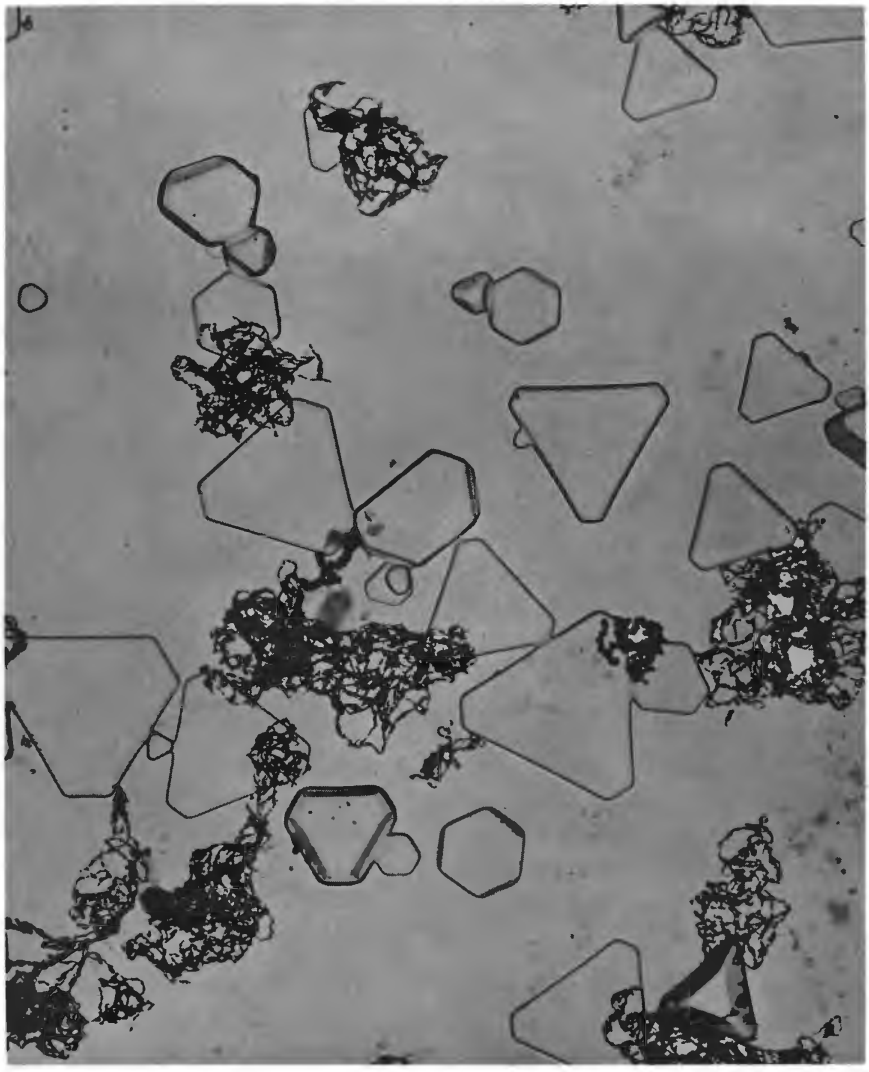


Figure 2. Most of these silver bromide grains from a photographic emulsion are flat plates, either triangular or hexagonal. After a moderate light exposure and complete development, some grains have been reduced to filaments of metallic silver but other grains are unaffected. (Carbon replicas, unshadowed, at 12,000 ×) (John F. Hamilton, Eastman Kodak Company)

M. von Ardenne[12] studied silver bromide crystals in the electron microscope. C. E. Hall and A. L. Schoen[13] found that the developed silver resembled a tangled mass of threads and ribbons, much like a mass of seaweed. The development of a grain started at certain centers, presumably the latent image centers. When the grains were fully developed on a photographic plate, "the filaments are so closely packed that most of the grain is completely opaque with filamentary structure in evidence only around the edges. Occasional filaments reach out far beyond the original crystal boundaries so that they may penetrate a neighboring crystal and render it developable." Filaments may be considered as silver crystals that are growing primarily in one direction only. From extremely small crystals, such as those in Lippmann emulsions, only one filament may emerge. (See Figure 3.) The degree of compression of the mass of filaments from a crystal depends on the softness of the gelatin encapsulating the crystal. The nature of the developing solution and its temperature also affect the compressive forces that the gelatin exerts upon the filamentary mass.

All the commonly used developing agents, except *p*-phenylenediamine, produced filamentary silver when silver halide crystals were developed. Metol and Amidol produced fine filaments; hydroquinone gave coarse ones. A ferrous oxalate developer which did not contain a silver halide solvent produced filamentary silver. Highly solvent developing solutions, or physical developers containing soluble silver salts, formed clumps of closely packed particles of metallic silver but no filaments of silver. A *p*-phenylenediamine developer produced images composed of the compact silver particles that are typically formed by physical developing solutions.

Early stages of the growth of metallic silver during development have been followed with the aid of the electron microscope.[14–16] Walter E. Mueller[17] has reported that filaments of silver formed during the early stages of chemical development "do not consist of metallic silver initially. They contained dissolved silver halide or complexed material and are reduced to metallic silver halide or complexed material and are reduced to metallic silver later on in the process." Mueller[18] postulates that the latent image catalyzes a solvent action of the developer upon the silver halide crystal, producing a fine stream of dissolved or complexed material that emerges into the solution to form filaments. Such filaments are often branched. These findings have been supported by W. Gross,[19] who used a light microscope fitted with an infrared radiation source and an infrared-sensitive camera to observe the development of emulsion-coated cover glasses. The processed samples were then studied with the aid of a 100-kV electron microscope. This is similar to the technique used by Hans Eger[20] to record cinematographically the development of various photographic materials. W. Gross found at the beginning of chemical development that some filaments, often branched, looked like empty tubes

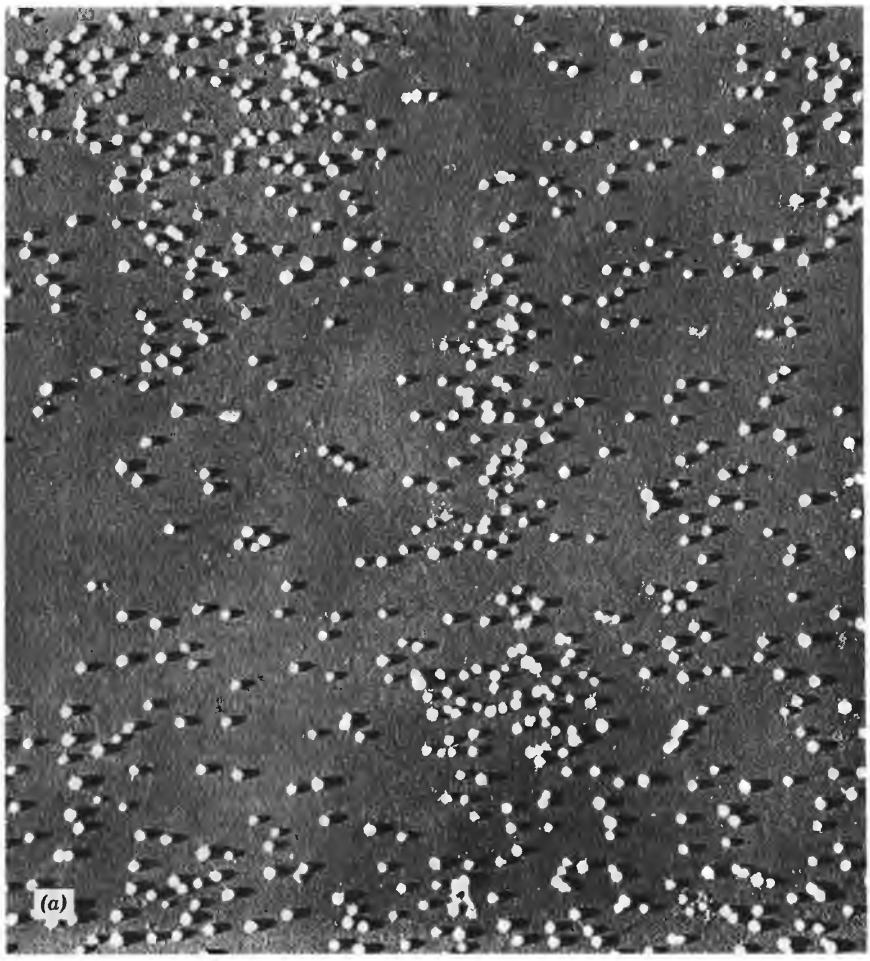


Figure 3. (*a*) Lippmann emulsions have extremely small silver halide crystals that (*b*) form a single filament after development. (John F. Hamilton, Eastman Kodak Company)

filled with silver bromide or some complex. This material was readily removable in fixing solutions. (See Figure 4.)

Direct observation of the results of development indicates that any mechanism of development must account for two kinds of image silver: the filaments arising from chemical development and the compact particles produced by physical development.[21–23] But the latent image cannot be observed nor can the reactions that distinguish between grains that differ

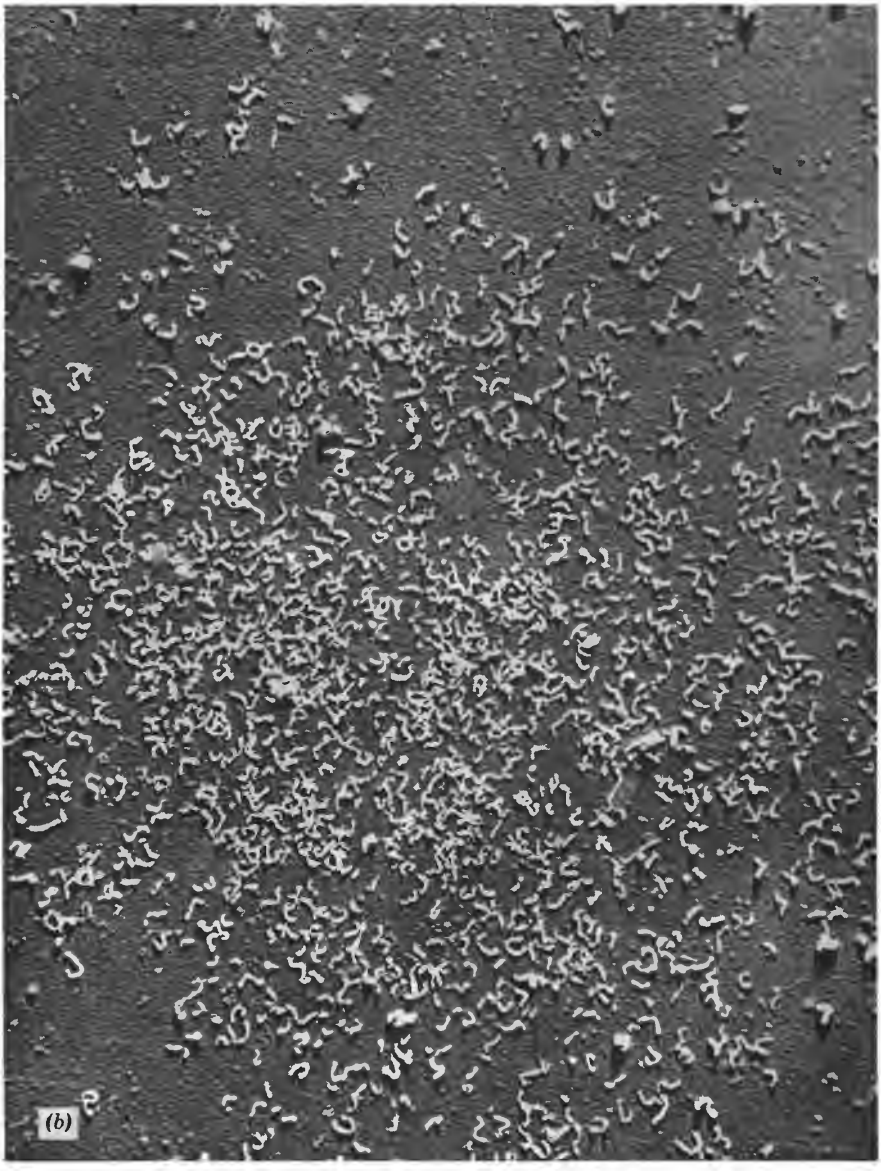


Figure 3. ***(continued)***

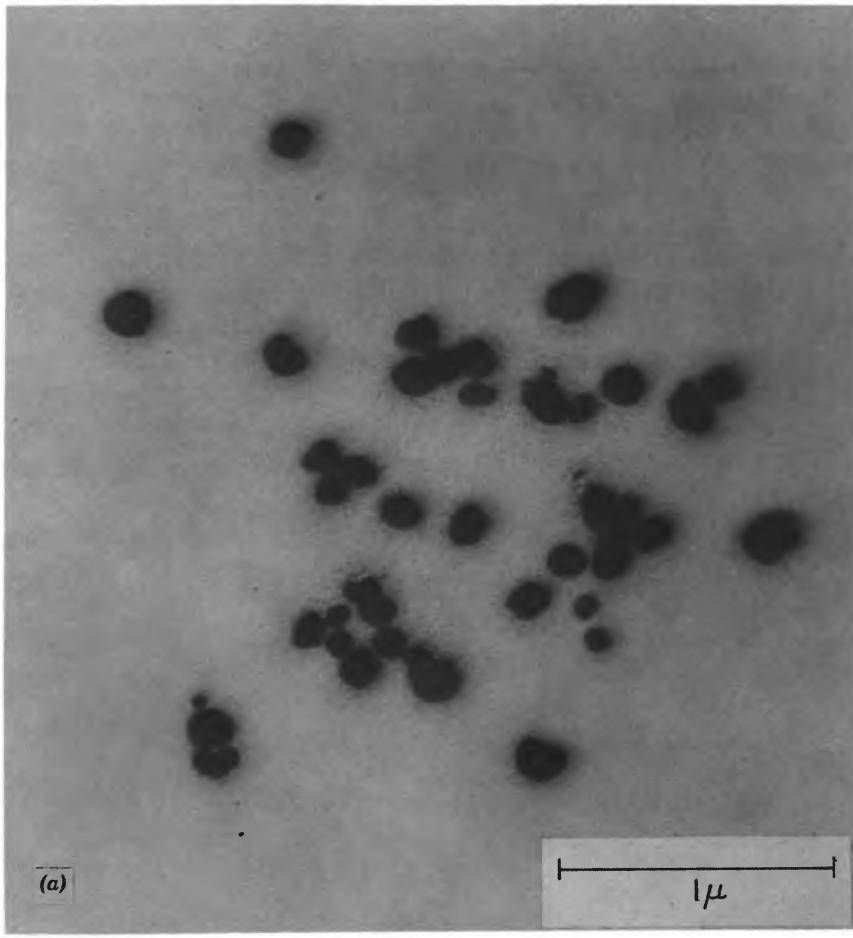


Figure 4. Electron micrographs of developed silver formed (*a*) by physical development and (*b*) by chemical development. [J. F. Hamilton, *App. Opt.*, 11: 15 (1972).]

only by a few atoms of silver located at discrete points on the crystal surface. No single mechanism of development has yet been devised that will uncontestably account for all aspects of chemical development. Possibly this failure to achieve a universally accepted mechanism for development is related to the failure to elucidate a completely satisfactory mechanism of latent image formation. Fortunately, the practice of photography does not depend upon a complete understanding of how the photographic process works.

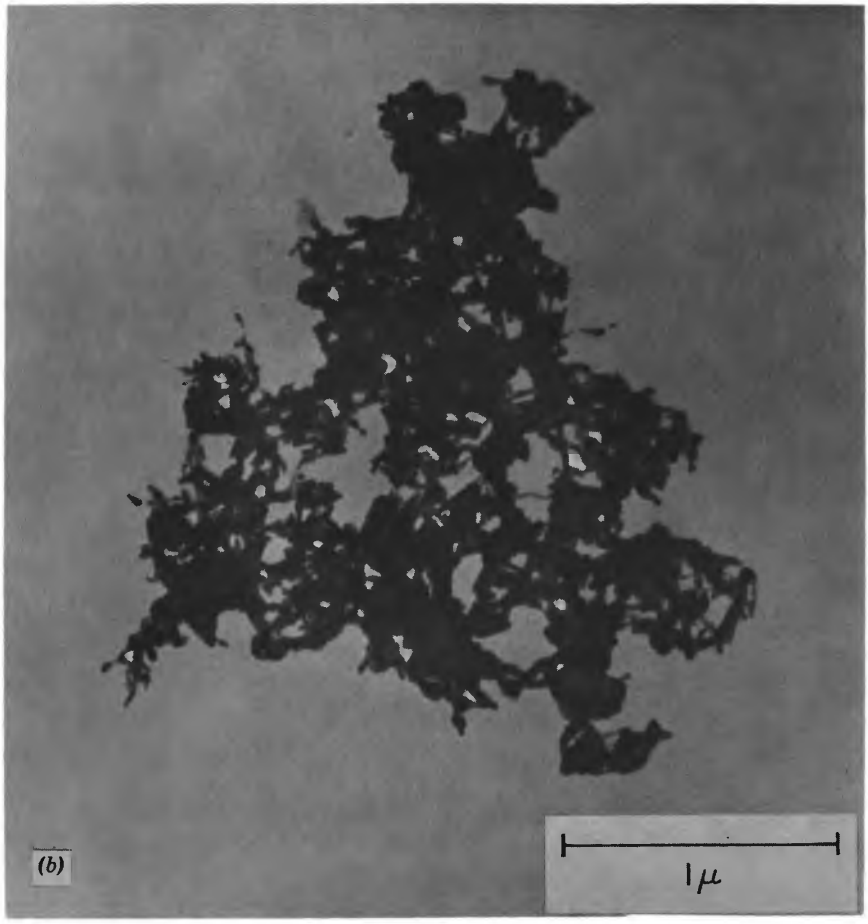


Figure 4. (*continued*)

DEVELOPMENT CENTERS

The developability of exposed silver halide crystals depends upon the existence in or on the crystals of certain areas from which reduction by the development agent takes place. These reduction or development centers appear to be composed, at least in part, of a substance that resists chemical attack more than silver halide or metallic silver.[24] A developable latent image speck has been estimated to contain as few as eight atoms of metallic silver.[25,26] A latent image containing 108 silver atoms is of the same order of magnitude as the resolution of the electron microscope.[27] The undeveloped latent image, therefore, formed by a normal light exposure

cannot be detected by present-day electron microscopical techniques. The latent image can be enlarged to a resolvable size by depositing gold upon the silver atoms of the image. Gold physical development was used by H. Hoerlin and F. A. Hamm[28] to treat the latent images formed by alpha particles, X-rays, and blue light on a double-coated, fast negative, bromoiodide emulsion of high contrast. Latent image centers of different sizes were produced by the different types of exposure. Hoerlin and Hamm found that "High-intensity alpha-particle and x-ray exposures produce a very large number of finely dispersed centers; irradiation with light of optimum intensity and 1/100 second duration forms a small number of centers; only very few specks result from exposures to light of very low intensity."

The iodide content and distribution in emulsion grains has been found to cause differences in the amount of distribution of the latent image centers.[29,30] Irradiation of microcrystals of silver iodide in an electron micro-

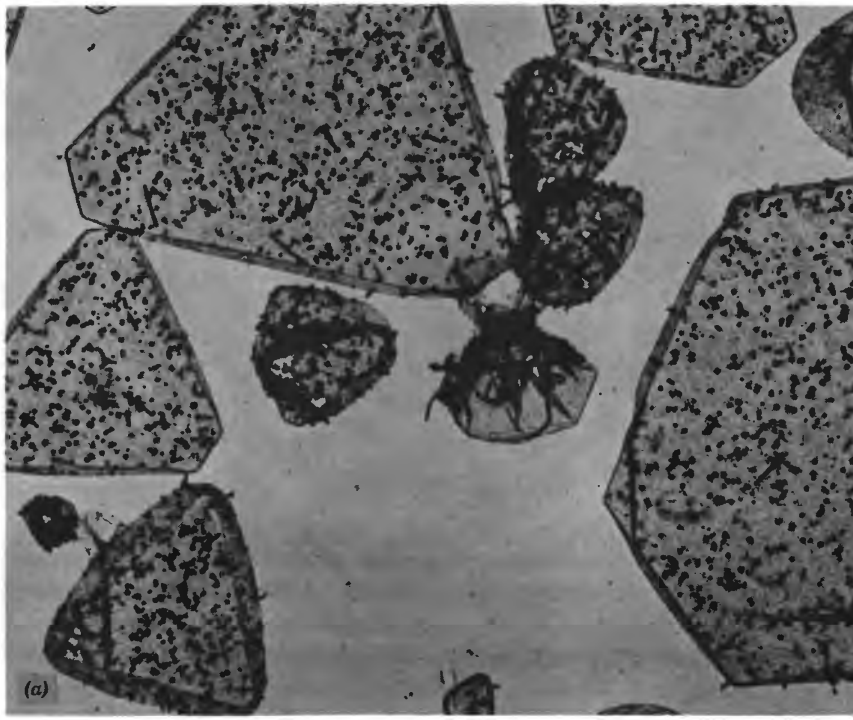


Figure 5. (*a*) High-intensity exposure produces many scattered surface development centers. (*b*) Low-intensity exposure gives a few large development centers on the grain surface. (John F. Hamilton, Eastman Kodak Company)

scope produced growth of silver filaments that arose from the region nearest the crystal surface with the tip of the filament remaining unchanged.[31] Exposure experiments upon silver halide crystals in an electric field were used by E. Klein and R. Matejec[32] to show the presence of interstitial silver ions in the crystal that contribute to latent image formation. The latent image centers were then enlarged by physical development so that the number of development centers per crystal could be determined in the electron microscope. At first the number of development centers per grain increased with increasing flash exposure. Continued exposure caused the number of centers to decrease but become larger. Equal amounts of light incident with different intensity produced different numbers of development centers per grain. Heavy exposure of silver bromide crystals produced silver filaments. The photolytic silver filaments are presumed to be formed by a mechanism similar to that of chemical development, although internal latent image may play a greater role with silver formed by continued light exposure.[33] (See Figure 5.)

Using pure silver bromide grains and very dilute developing solutions, W. F. Berg and H. Ueda[34] studied the distribution of development centers on

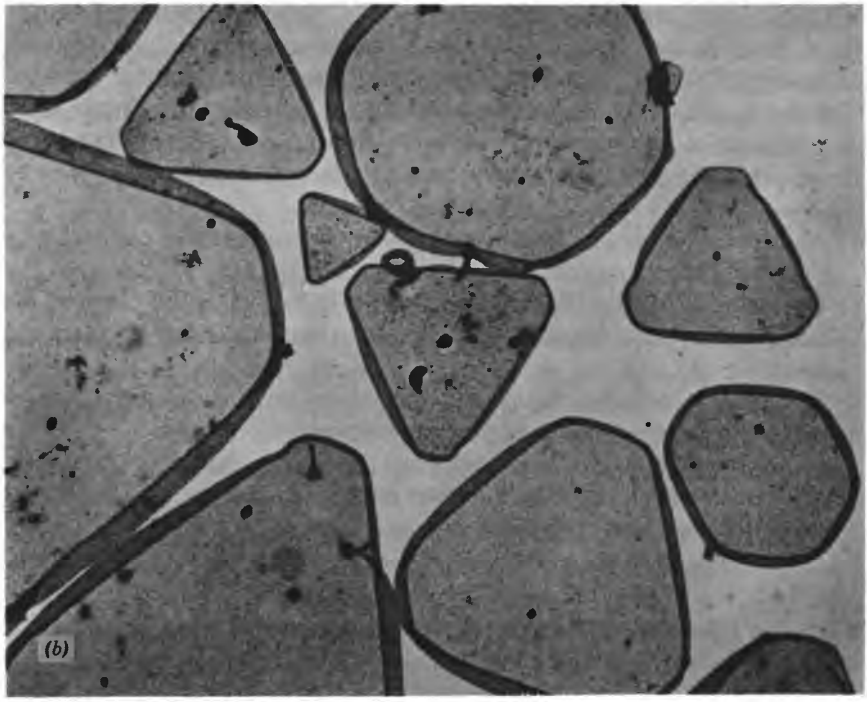


Figure 5. (*continued*)

single grains. Berg and Ueda reported that "With low-intensity exposures, developed silver specks produced with surface developers appeared scattered when the exposure time was short; and they tended to be situated in the centres of the tabular grains when the exposure time was long. The silver specks resulting from internal developers appeared both in the central and surrounding parts, sometimes in rows. Thus, the locations of internal and superficial development centres do not seem to be related." High-intensity exposures produced many scattered surface development centers.

Development centers that formed along grain edges appeared to be fog centers. Silver and silver sulfide, formed during the chemical finishing of the emulsion grains, are thought to be deposited in surface defects.[35] Such centers capable of initiating development of a crystal as fog would be deposited over the surface area. The probability of fog development should thus increase with increasing surface area of the crystal but, in fact, as indicated by G. C. Farnell,[36] "Although total numbers of centres per grain are proportional to area, the effective numbers are proportional to mean linear grain dimension. The association of development rate as fog with edge length is supported by the fact that fog development centres are found to occur largely on grain edges."

Development centers, according to K. V. Chibisov and Zh. L. Broun,[37] must have catalytic activity, electron-accepting capacity, and electron conductivity. Sufficient free silver ions must also be present near a center. Yet, the latent image may not possess all the necessary properties for a development center, such as, for example, electron conductivity. These two investigators feel that the center is formed in the following manner:

1. Amorphous silver particles accumulate at certain preferred sites during the chemical ripening of the emulsion grains.
2. During exposure, the effect of the light is to increase the number of amorphous silver particles until metallic silver nuclei separate to form the latent image center.
3. The initial stage of development is to build up latent image silver nuclei to form an electron-conducting development center.
4. The development amplification process then begins, because the development center can grow freely into silver particles in the presence of an ample supply of developer-supplied electrons and crystal-supplied silver ions.

SEQUENCE OF EVENTS DURING DEVELOPMENT

One method to gain an insight into the complexity of the development reaction is to separate it into a continuous sequence of steps. The develop-

ment of a single silver halide grain has been followed by many investigators, such as G. I. P. Levenson[38,39] or Walther Jaenicke and Claus Schott.[40] The following sequence of events was proposed by L. F. A. Mason[41] for a better understanding of the mechanism of development:

1. Approach of the developing agent to the surface of the grain.
2. Adsorption of the developing agent to the grain surface.
3. Transfer of an electron from the developing agent to the latent image site.
4. A. Conduction of the electron through the latent image speck.
   B. Having lost one electron, the developing agent may:
      (1) Give up another electron and desorb.
      (2) Dismutate into higher and lower oxidation products, the higher product being desorbed.
      (3) React with sulfite.
      (4) The primary developing agent may be regenerated by a second developing agent.
5. Combination of the electron with a silver ion from the grain.
6. Deposition of the silver atom to enlarge the latent image.
7. Movement of other silver ions through the grain toward the latent image site, leaving pits on opposite side of grain surface, where bromide ions are liberated.

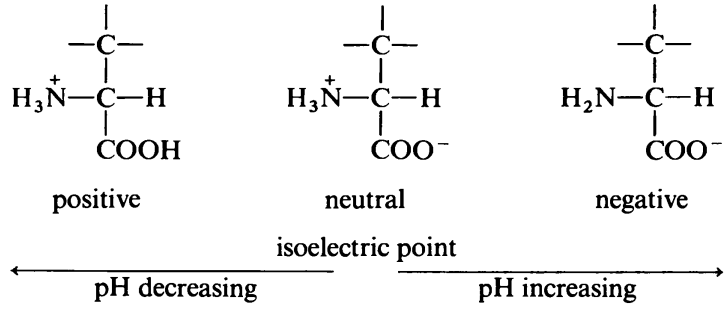
The net result of these steps may be expressed as a two-part relationship:

1. Developing agent → oxidized developing agent + electron.
2. Silver halide + electron → metallic silver + halide ion.

Approach of the Developing Agent to the Surface of the Silver Halide Grain

In the interior of a silver halide crystal each positive silver ion or each negative halide ion is surrounded symmetrically by six ions of the opposite charge to saturate the valence of each central ion. At the plane surface of the crystal, however, each ion is surrounded by only five ions of the opposite charge, leaving some attractive forces unfilled. Each ion in the surface layer still attempts to satisfy all its valences completely, as this state is the most stable. The silver ions of a silver bromide grain attract and strongly hold on the surface a layer of bromide ions near the sites of the silver ions. The negative bromide ions that are adsorbed would attract a like number of positively charged ions from solution, such as potassium ions; this attraction between bromide and potassium ions is much less than between the silver ions of the grain and the adsorbed bromide ions. A double layer of ions is formed over the surface where each silver ion is present.

Although electrical neutrality has been maintained by the adsorption of like numbers of the positive potassium and the negative bromide ions, the stronger attraction between the silver and bromide ions results in each grain's being effectively negatively charged. During the making of an emulsion composition, excess bromide ions may be deliberately added to secure grains with a negative charge, as this condition promotes improved photographic properties. In addition, the grains are formed in gelatin. The gelatin encapsulates each silver bromide grain, being absorbed to the grain surface. Gelatin, composed of amino acids, is electrically neutral only at its isoelectric point. In an alkaline developing solution, gelatin is negatively charged.[42]



The negative charge of adsorbed halide ions and gelatin molecules constitutes a negatively charged barrier that envelopes the grain, repelling other negative ions. This force of repulsion may be reduced somewhat by using a considerable quantity of a neutral salt in an alkaline developer. The presence of strongly adsorbed, positively charged organic molecules, such as quaternary salts, helps reduce the repulsion of the negatively charged barrier, producing accelerated development.

The charge barrier surrounding the grains has been used by T. H. James[43,44] to explain the delay exhibited by negatively charged developing agents before the development of the latent image begins. This delay before a measurable silver image is produced is called the induction period. A developing compound that can act as a neutral molecule does not exhibit an induction period, but all negatively charged developing ions do. James has shown that the induction period increases with increasing negative charge on the ion. It has been concluded that the induction period is not a function of the nature of the developing agent but only of the charge on its active reducing form. The more negative the charge on the active ion, the greater the length of the induction period. James has found that developing agents may be classed according to ionic charge, with uncharged molecules having no induction period and triple negatively charged molecules having the longest time before

Table 1. Classification of Developing Agents

Type of Developing Agent	Charge on Active Particles			
	0	−1	−2	−3
Hydroquinones			Hydroquinone	Sodium hydroquinone monosulfonate
p-Aminophenols		Metol *p*-Aminophenol	*p*-Hydroxyphenylglycine Metol monosulfonic acid	
p-Phenylenediamines	*sym*-Dimethyl-*p*-phenylenediamine *p*-Aminodiethylaniline Diaminodurene 2-Amino-5-diethylaminotoluene	*p*-Aminophenylglycine		
Others	Phenidone	Hydroxylamine Phenidone	Pyrogallol Ferrous oxalate	

the appearance of a photographic image. Such a classification is shown in Table 1, derived from the work of James.[43]

In 1942 T. H. James and G. Kornfeld[45] described the charge effect as follows:

> The repelling force exerted upon an approaching developer ion by the negative charge of the adsorbed halide layer will be proportional to the charge of the ion itself. Only a fraction of the negatively charged ions will possess sufficient kinetic energy to overcome this repulsion, and the percentage will decrease rapidly as the charge increases. Those ions which, by virtue of their excess kinetic energy, approach closely enough to the latent image centers and which, in addition, possess sufficient activation energy, will react to produce metallic silver. As the silver speck grows in size, the protective layer becomes more and more disrupted in this region. The resulting decrease in charge permits an increase in the effective concentration of the developing agent at the reaction zone, and hence an increase in the reaction rate. The greater the charge of the developing ion, the greater will be the relative increase.

The effect described will be pronounced only in the early stages of development of the individual silver halide grains, and will probably disappear before the silver speck becomes very large. As expected, increase in the concentration of excess bromide ion has a greater effect upon the induction period of the charged developers than upon the subsequent reduction rate . . . and the greater the charge of the developing agent, the greater is the relative effect upon the induction period.

According to the views of L. F. A. Mason,[41] however, the charged layer surrounding the grain is severely contracted in a normal developer; in fact, the thickness was calculated to be about that of a single layer of ions. In this situation, negative developing ions should suffer no electrostatic impedance in their diffusion to the grain surface. Mason states, "Charge barrier effects cannot affect the concentration of developing species at the grain surface under normal development conditions, the approach of the developing ions to the grain surface being unaffected by their ionic charge." Mason's view would imply that the charge effects observed by James are more related to the adsorption of the developing agent to the grain surface rather than to their approach to the grain.

Induction Period

"All this indicates that the nature of the induction period appears to be more complex than interpreted at present," concluded V. A. Veidenbakh and P. I. Levina.[46] Other factors besides charge effects may influence the time before the metallic silver of the image is being formed at a steady rate. When the photographic material is first immersed in the processing solution, there is a delay that involves the diffusion of the chemical ingredients into the gelatin layer. The ingredients of a developing solution diffuse at different rates. Hydroxyl ion has been found to penetrate more slowly than developing agents at the pH and chemical concentration of normal developers because the hydroxyl ion is consumed by the gelatin. H. Iwano[47] has stated that "The results from direct comparison of penetration of developing agents and OH^- in the same emulsion layer under diffusion-controlled development showed that higher swelling, lower hardener content, and higher AgX concentration proved more favorable to the reduction controlled by penetration of the developing agent, rather than by that of OH^-."

Developing agents penetrate faster through emulsion layers than through gelatin layers, and through unhardened gelatin layers more quickly than through hardened gelatin layers.[48] Hydroquinone diffused the slowest, Phenidone was faster, and Metol was the fastest. A large percentage of hydroquinone may be reversibly adsorbed to the gelatin, thus increasing its diffusion time. Increasing the pH and increasing the concentration of the

developing agent increases penetration rate and shortens the induction period. Concentrated solutions of hydroquinone at high pH have a shorter induction period than less concentrated solutions at lower pH values. The reduction of silver halide by the developing agent has been said[49] to begin "at a smaller pH value in the emulsion layer than the pH value in the developer."

P. I. Levina[50] has written that

> The induction period depends, within the region of higher pH values, upon the number and position of the negatively charged active groups in the anion of the developing agents but at lower pH values upon the chemical nature of these groups and their active concentration. Thus, singly charged developing agents, with previously determined potentials (Metol, para-aminophenol), and doubly charged developing agents with the arrangement of active groups in ortho position (catechol) within the largest range of the pH values used develop with the smallest and almost uniform induction period. The doubly charged developing agents with the arrangement of active groups in the para position (hydroquinone, Glycin) have the highest induction period at uniform potentials. An intermediate position is occupied by pyrogallol, containing three active groups, which are concentrated in one end of the molecule. It has been noted that para-phenylenediamine occupies a special position. In a weakly alkaline medium up to pH 10, when the development is provided for nondissociated amino groups, the induction period does not depend upon the pH value. A further decrease in the induction period when the pH value is increased was explained by the formation of the anion of para-phenylenediamine as a result of an acid dissociation of amino groups.

Exposure level influences the induction period. Extreme exposure has been reported[51] to reduce the induction period of hydroquinone developers by a factor of 3.6. Gelatin plays a role in the induction period.[52] Hydroquinone has been found to diffuse into gelatin faster than it diffuses out.[53] Gelatin does not retard the development by *p*-phenylenediamines and, in fact, may accelerate development by the uncharged developing agent. The gelatin layer helps depleted developing agents and alkali, and released bromide, to accumulate in the emulsion, retarding the total process. The accumulation of oxidized hydroquinone (semiquinone) accelerates the development reaction, particularly with a low concentration of sulfite.[54] The presence of accelerating or decelerating ions at the site of development influences the induction period. Negative-charged ions that are absorbed on the silver halide or latent image sites, such as bromide ion on silver halide, inhibit the development by negatively charged developing agents, such as hydroquinone. The accumulation of bromide ions forms a more compact negative double electric layer which is a more severe obstacle for double-charged ions, such as hydroquinone, than for single-charged Metol ions.[55]

Positively charged ions, such as quaternary salts, often shorten the induction period of negatively charged developing agents.[56] Phenylmercaptotetrazole increases the induction period for most developing agents, apparently through interference with both chemical and physical development.

Adsorption of the Developing Agent to the Grain Surface

The presence of the latent image is not the cause of the reduction of a silver halide grain to metallic silver. The latent image does not cause any reaction to occur that would not occur without it; the latent image does cause an exposed silver halide grain to be developed in less time than an unexposed grain. If development is extended for a sufficient time, all the silver halide grains will be converted to silver. The few silver atoms of the latent image are the catalyst that accelerates the development of the exposed grain. It is to these catalytic nuclei that the developing agent must transfer its electrons, but just how this is done is still a subject of lively controversy.

The developing agent must transfer its electrons, but the moot question is where: to the silver halide crystal, to the silver of the latent image, or to the interface between the latent image and the silver halide of the surrounding grain? S. E. Sheppard and G. Meyer[57] proposed in 1919 that "Complex formation will consist essentially in actual chemical combination of the surface silver halide molecules with molecules of the reducer, the valences of the surface molecules of the silver halide being less saturated than those of the interior." It was also noted that the developing agent might be adsorbed to the grain surface without chemical combination. These authors conjectured that the complex might occur between the positively charged silver ion of the grain and the negatively charged developing ion or between the uncharged free base of the organic reducer and the silver halide. At the pH of a developing solution, such complexes would be unstable, yielding oxidized developer and, as the result of the electronic transfer, metallic silver.

In a discussion of the mechanism of chemical development T. H. James[58] concluded: "In development by most agents, adsorption of the developing agent *by the silver halide* or at the silver–silver halide interface appears to be of major importance in determining the rate of development." Complex or salt formation between the silver ion and the developing agent is thought to result when the developing agent is adsorbed by the silver halide. Developing agents containing hydroxy groups can form salts between the ionized hydroxy group and a silver ion of the grain. Amino-containing developing agents can form complexes between the amino group and the silver ions.

Once formed, the salt or complex need only undergo electronic rearrangement to produce a silver atom and an oxidized developer molecule. But the rearrangement requires an activation energy; that is, some energy must be supplied or the rearrangement cannot occur. The energy needed in the presence of the catalytic influence of the latent image is considerably less than for silver halide grains without the latent image silver. The silver ion–developer salt or complex is thus more easily decomposed on exposed grains than on unexposed grains, resulting in the preferential reduction of those grains first.

James[58] states, "The rate-controlling step in fog formation in the unsensitized emulsion appears to be the 'uncatalyzed reaction' between the silver ions and the developing agent." If the energy required for the uncatalyzed reaction is very low, the developing agent in the adsorbed complex will show little power of selective development. The catalytic effect of a latent image site is not needed to lower the energy of the electronic transfer, and silver halide is reduced indiscriminately.

The electron transfer has been proposed to occur at a triple interface: silver, silver halide, developer solution. James[59] has suggested that this is the most favorable location for reaction, as the silver ions are already subjected to adsorption forces and are probably displaced slightly from their normal lattice positions. A complex can be formed at this site that "can be considered as the transition state between Sheppard's 'adsorption complex' and the ultimate reaction products—silver and oxidized developer."[60] The action of antifogging agents and other strongly adsorbed material, such as gelatin or dyes, would either decrease the availability of silver ions or interfere with the formation of the complex, an action that is normally encountered in practice.

Adsorption of the developing species to the silver halide surface would occur on all grains but, in the absence of the latent image speck, the reaction between silver ions and the developing agent would be very slow. Fog centers may indeed resemble latent image centers, but fog centers are inferior in catalytic activity.[61] Silver reduction at a fog center would require a greater amount of energy, resulting in slower development and a greater inhibition of that development by ions that compete for the available adsorption sites, such as bromide ions or organic antifoggants.

Considerable research has been done to determine if developing agents are adsorbed and just where the preferred site is located. L. E. Oppenheimer and T. H. James[62] reported that no adsorption of negatively charged developing agents by negatively charged silver halide surfaces was observed. The *N*,*N*-dialkyl-*p*-phenylenediamines are more strongly adsorbed to silver bromide than the corresponding *p*-aminophenol derivatives.[63] The addition

of water insoluble groups, such as $-CH_3$, increases the absorptivity, and the addition of water-solubilizing groups, such as —OH, decreases adsorptivity. The addition of $-NH_2$ increases adsorptivity considerably. With a number of *p*-aminophenols and *p*-phenylenediamines it has been concluded[64] that "The rate of silver growth during the induction process is determined solely by the solution concentration of each developer and its half-wave electrode potential. The adsorption of the developers does not play a rate-determining role in this process. These findings support the view that the induction process is an electro-chemical process without adsorption." The active ion for various hydroquinones was found to be the double negatively charged ion, but the adsorption of the developer ion was not an important factor in determining the rate of the induction period.[65] D. C. Shuman and T. H. James[66] have concluded, "Clearly, adsorption is not the determining factor controlling the rate of development."

The adsorption of developing agents to metallic silver has been measured.[67] (See Table 2.) 4-Amino-3-methyl-*N*,*N*-diethylaniline and 4-amino-3-methyl-*N*-ethyl-*N*-(β-methylsulfonamidoethyl)-aniline were reported to be more strongly adsorbed than *p*-phenylenediamine or Metol. Adsorption of hydroquinone by silver was not detected. The adsorption of 1-phenyl-5-mercaptotetrazole to a metallic silver surface has been found to consist of a single monolayer covering the entire silver surface.[68] Only 10 to 15% of the surface was covered by benzotriazole. When the metallic silver surface is covered by an insulating layer of the phenylmercaptotetrazole, the transfer of electrons from the developing agent to silver ions is inhibited. Retardation of development applies both to the *p*-phenylenediamine developing agents (which adsorb to silver) and Metol-hydroquinone (which adsorb weakly, if at all), implying that adsorption of silver ions to silver may be prevented in some measure.

V. I. Saunders and W. West[69] have proposed that electrons from the developing agent may pass to the surface of unexposed silver bromide crystals, then are ejected from shallow traps and migrate to internal fog centers to form developable centers if a solvent developing solution is used. This injection of electrons into silver bromide has been questioned by Walther Jaenicke,[70] who maintained that "development only is possible via surface centers."

Surfactant Classification of Developing Agents

Developing agents have been classified by structure and other means,[71,72] but according to J. Q. Umberger[73–75] may be classified by their adsorption to the catalytic sites. (See Figure 6.)

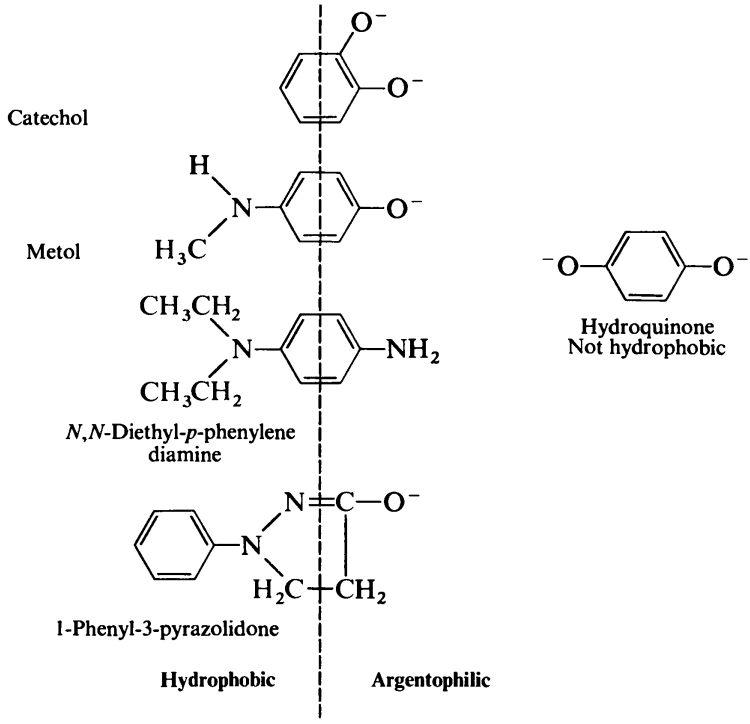
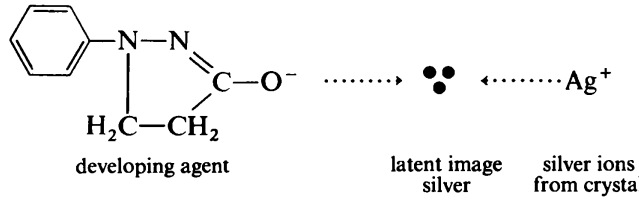


Figure 6. Developing agents may be classified by their adsorption to catalytic sites. The strength of adsorption is determined by the surfactant nature of the molecule of the developing agent.

The critical complex for photographic development, using Phenidone as the developing agent, is as follows:[73]



The argentophilic end of the developing agent is attracted to silver of the latent image, and the other, the hydrophobic end, has low water solubility, forcing the molecule to leave the water of the solution. These conditions promote the adsorption of the developing-agent molecule to form the critical complex so that electron transfer may be readily accomplished. The Phenidone molecule has low solubility except when alkali causes the ionization of

Table 2. Adsorption[a] of Developing Agents by Silver[96]

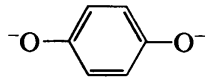
Developing Agent	Adsorption (μM/m^2) pH 8.3[a]	pH 10[b]	pH 10.85[b]	pH 10.8[c]
Hydroquinone	Undetected	0.5	0.5	0.25
Methylhydroquinone	0.3	0.6	0.8	1.1
Ethylhydroquinone	1.3	1.1	1.4	
n-Butylhydroquinone	1.2	1.2	1.0	1.45
t-Butylhydroquinone	1.2	1.4	1.2	
Hydroquinone thiosulfonate	1.5	2.9		
Catechol	1.3			
Metol	1.0	0.9	0.25	
p-Phenylenediamine	1.0	1.4	1.4	
Diaminodurene	0.6	1.6	0.9	
CD-2[d]	0.8	1.3	0.7	
CD-3[e]	0.5	1.0	0.8	
Phenidone	0.7	1.3	1.6	
p-Hydroxyphenylglycine	No adsorption detected			

[a] Values given are for saturation, which was attained at developer concentration of 0.2 to 0.6 millimole/liter.
[b] Adsorption to colloidal silver; data by D. C. Shuman.[66]
[c] Adsorption to silver powder; data by Willems and van Veelen.[76]
[d] 4-Amino-3-methyl-*N*,*N*-diethylaniline hydrochloride (Kodak Color Developing Agent CD-2).
[e] 4-Amino-3-methyl-*N*-ethyl-*N*-(β-methylsulfonamidoethyl)aniline hydrochloride (Kodak Color Developing Agent CD-3).

one end. When this negatively charged end is attracted to silver, the remainder of the molecule is essentially insoluble. This condition makes for a very strong adsorption, capable of displacing ions that might already be present on the silver halide grain. In the case of Phenidone, bromide ion exerts very little antifoggant action, as the Phenidone ion may replace it. Strongly adsorbed organic antifoggants are needed to restrain developers containing Phenidone. Antifoggants may be considered to be in direct competition with the developing agents for adsorption sites on the grain surface. The nature of the anti-

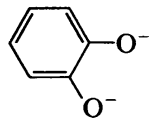
foggant is thus directly related to the adsorption strength of the developing agent.

Hydroquinone in the doubly charged form,



is argentophilic at either end of the molecule. When one end is adsorbed to the grain, the other end still possesses high water solubility. If conditions permit, this end may also be attracted to the grain surface, causing the molecule to be adsorbed flat on the surface. Other developing agents with argentophilic and hydrophobic ends are adsorbed end-on; that is, the molecules are parallel to each other and stacked like a deck of cards. Doubly ionized hydroquinone molecules tend to stay in solution rather than in the adsorbed state that is necessary for the critical complex formation of development.

Catechol in alkaline solution would exist as



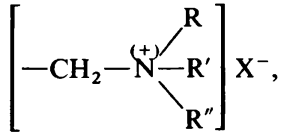
possessing a strong argentophilic end where the ionized hydroxy groups are. The rest of the molecule would be highly water insoluble. Catechol should adsorb more strongly than hydroquinone and be more capable of forming the critical complex for electron transfer. In practice, catechol develops more rapidly than hydroquinone.

The addition of water-insolubilizing groups, such as alkyl groups, may help to make one end of the molecule more insoluble. This end of the molecule becomes more hydrophobic and the developing agent molecule is more strongly adsorbed.[76] Metol and *N*-alkylated-*p*-phenylenediamines are more strongly adsorbed than the unsubstituted parent molecules. Metol and the *N*-alkylated-*p*-phenylenediamines are capable of more rapid development than *p*-aminophenol or *p*-phenylenediamine because their stronger adsorption makes more readily possible the formation of the critical complex for development.

Because it is so poorly adsorbed, hydroquinone exhibits a long induction period before the reduction of silver can begin. Quaternary salts have molecules that possess argentophilic and hydrophobic ends of the molecule. Quaternary salts are strongly adsorbed to silver. The adsorption of hydroquinone by metallic silver in the presence of a quaternary salt, such as benzyldimethyldodecylammonium bromide, has been studied by H. D.

Meissner.[77] The doubly ionized hydroquinone anion was found to form a complex with the quaternary compound. This complex was strongly adsorbed to silver. The presence of the quaternary salt in a hydroquinone developer then shortens the induction period of a hydroquinone developer, because the complex of the two is capable of stronger adsorption than the hydroquinone alone. However, for a developing agent that is normally strongly adsorbed, such as Phenidone, the competition for adsorption to suitable sites between the quaternary salt and the developing agent results in a slight retardation of development, as shown when the quaternary salt is added to a pure Phenidone developer.

Another approach to speed the development of hydroquinone was used by J. F. Willems.[78] He studied the effect of the introduction of one or two positively charged groups on the hydroquinone molecule. These groups were of a quaternary nature,



where the R groups are alkyl groups, such as $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2OH$, or others. The presence of positively charged groups on hydroquinone decreased considerably the induction period normally observed with hydroquinone development. These groups on the negatively charged hydroquinone molecule were found to diminish the electrostatic repulsion by the negative charge barrier and to increase the ease of adsorption of the molecule on the silver halide surface.

Conduction of the Electron Through the Latent Image Speck

In the catalysis theory of development, the activated complex of latent image silver–developer–silver ion at the surface of the latent image breaks down into a metallic silver atom and the oxidized form of the developing agent. The silver atom enlarges the latent image. In 1938 R. W. Gurney and N. F. Mott[79] proposed a theory of development that bears their names. The latent image silver was believed to act as an electrode, with the anodic side against the developer solution and the cathodic side against the silver halide of the grain. The active species of the developing agent supplies an electron to the metallic silver latent image speck, this electron then being conducted through the electrode until it reaches the point of contact with the grain. Here, the electron and a silver ion combine to form metallic silver that enlarges the latent image.

This theory is called the electrode or electrochemical theory of development. (See Figure 7.)

The electrode theory of development separates the site of electron transfer from the site of silver reduction, the developing agent never coming in contact with the silver ions of the grain. H. Baines[80] built a cell consisting of two test tubes, one containing a developing agent with sodium sulfite and sodium carbonate in the solution, the other containing the same concentrations of sodium sulfite and sodium carbonate but without the developing agent. One end of a silver wire was immersed in the tube containing the developing agent and the other end of the wire, first treated with bromine to form silver bromide, was dipped in the solution without the developing agent. The two solutions were joined by a salt bridge. After two hours, the silver bromide on the wire had been reduced to metallic silver.

No direct contact between the developing agent and the silver ions had been necessary to produce metallic silver. In the first solution, the developing agent had supplied an electron to the silver wire. This electron was conducted to the other end of the wire, where the silver bromide was reduced to metallic silver. Proponents of the electrode theory suggest that in this model experiment the silver end of the wire is the anode and the silver bromide end is the cathode of a galvanic cell that would approximate the function of a latent image site on a silver halide grain.

The silver of a latent image site would serve to catalyze the transfer of electrons from the developing agent, promoting development first of the exposed silver halide grains. The structure of the developing agent determines the rate of electron transfer, the ortho and para benzene compounds being oxidized but not the meta-oriented compounds. The surface condition of the silver speck (latent image) would also be a factor in the electron transfer.

The transfer of the electron from the developing agent to the silver nucleus is thought to be slower than the rate of reduction of silver ions at the nucleus; the presence of the silver nucleus reduces the energy necessary to cause electron transfer. G. P. Faerman[94] summarizes the selective action of electrochemical development by stating, "The rate of discharge of Ag^+ ions on centers of development (cathodic process) is higher than the rate of transfer to it of electrons from the developing agent (anodic process). These speeds depend on both on the energy of activation of the anodic and cathodic processes and on the concentration in solution of Ag^+ ions and the reduced and oxidized forms of the developing agent."

In physical development, especially after the fixation of the silver halide, only the silver nuclei produced by exposure remain in the gelatin layer. Certain sites on the surface of the silver nuclei are thought to be more reactive than others. According to the ideas of James, a complex of the developing species and Ag^+ ions from the solution are adsorbed to these sites. This

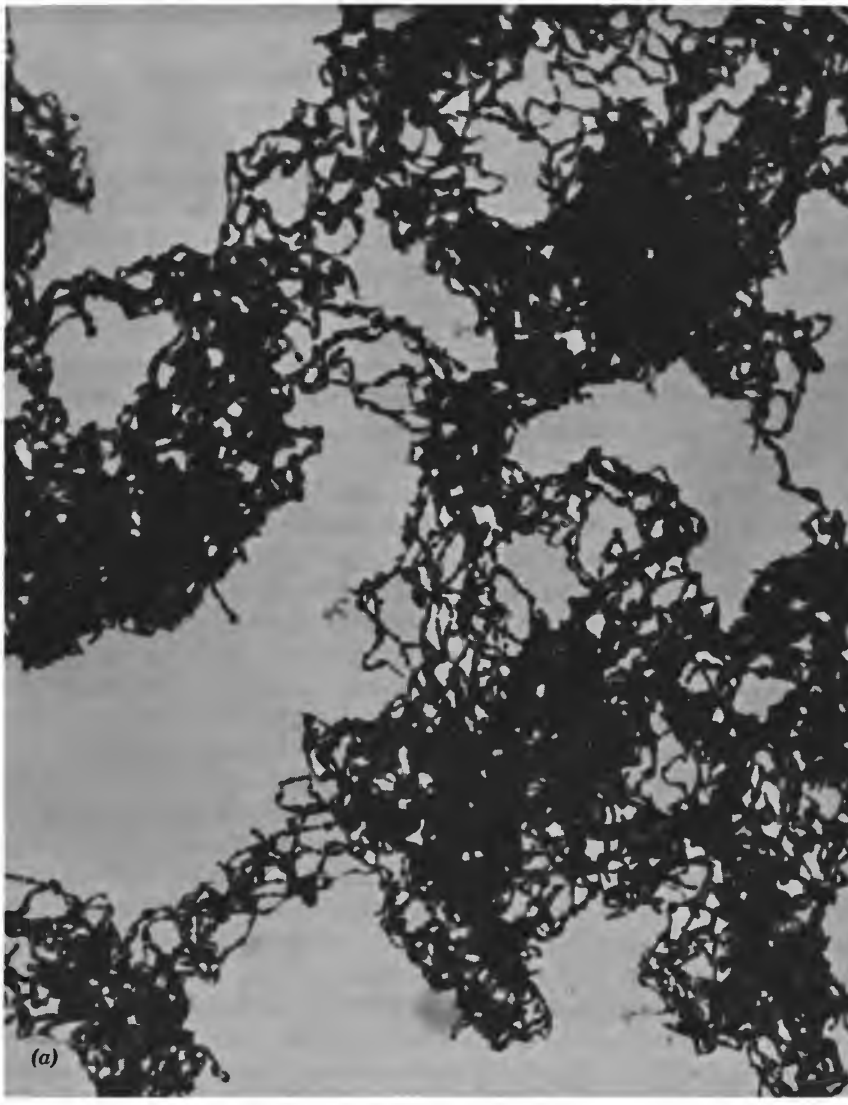


Figure 7. (*a*) **Developed silver (chemical) consists of a mass of silver filaments, but at greater magnification (*b*) linear features within the filaments are discernible. [J. F. Hamilton, *App. Opt.*, 11: 16 (1972)]**

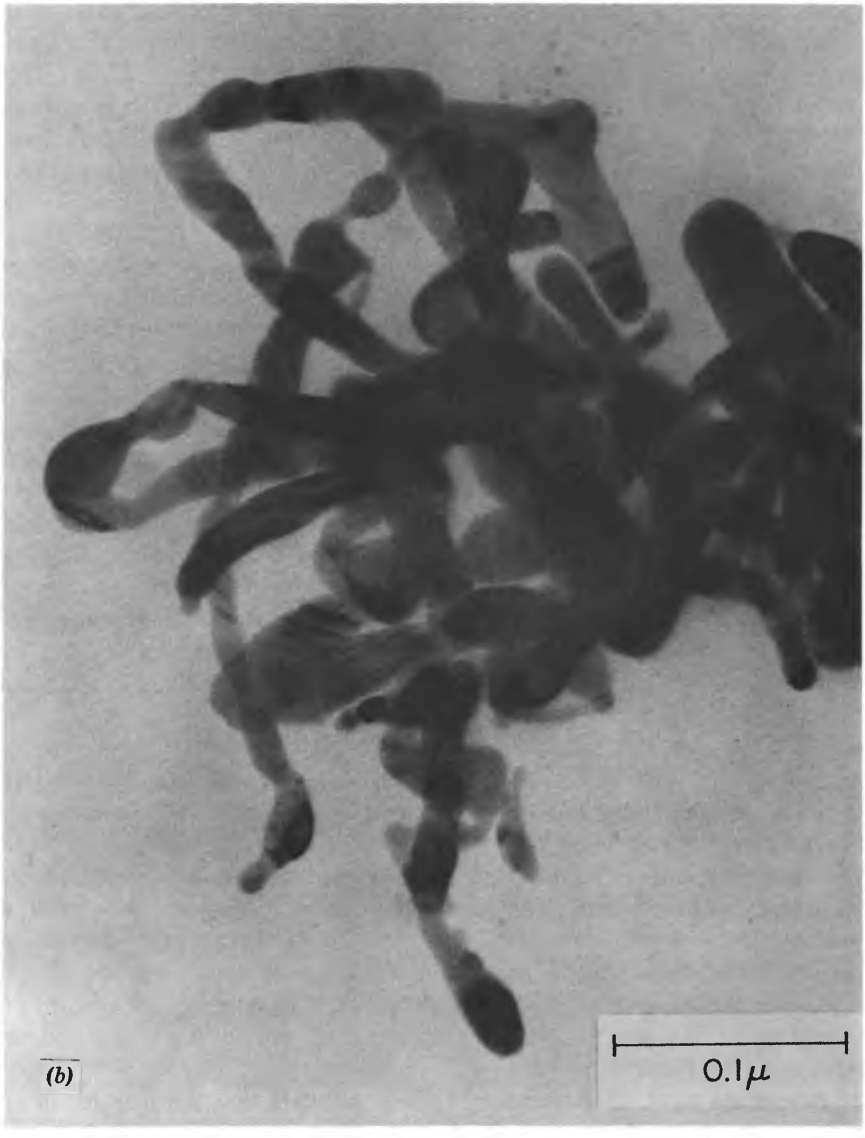


Figure 7. (*continued*)

adsorbed complex then dissociates into the oxidized developing agent and an atom of silver. The continued addition of atoms of silver causes the microscopic latent image nuclei to grow into a visible metallic silver image. This silver is of a compact form and not filamentary in nature. The essentially spherical particles produced by physical development may, however, have irregular surfaces. Filamentary silver has been reported during physical development.[81]

The electrode theory of the development mechanism has attracted the support of a number of research scientists.[82–90] Others believe that the adsorption complex at the triple interface provides a better explanation of the mechanism of development. This, as W. F. Berg[91] notes, "is the clearest indication of our lack of understanding." Berg sees that "there would seem to be no inherent contradiction between the electrode theory and one that stresses adsorption phenomena on a triple interface." T. H. James and John F. Hamilton[92] conclude that although experiments on electrode and triple interface mechanisms "have added to our knowledge of how development *might* occur, they do not establish whether these mechanisms provide the most rapid way for development to occur or that it actually occurs by these processes. What we really need is a definitive experiment that would decide between the 'electrode theory' and the 'complex formation theory' of development, but the design of that experiment remains for some future inspiration." The statement by Walter Clark[93] that begins this chapter was made in 1922 and would seem to be true today.

Growth of Silver on the Latent Image Site

Development occurs by the formation of an adsorption complex of the developing molecule and silver ions at the edge of the latent image where it contacts the silver halide of the grain (catalysis theory) or by the formation of an adsorption complex of the developing molecule upon the active sites of the silver of the latent image (electrode theory). The lifetime of the adsorption complex is very short, producing an oxidized developing agent and an electron. (See Figure 8.)

According to V. I. Sheberstov,[94] "It is possible that the transfer of an electron from the developing agent to the Ag^+ ion has a place within the bounds of the active complex. But it is also possible that the developing agent undergoes chemical change (passing from the benzenoid to the quinoid) in the bounds of the active ensemble, transferring a released electron to the metallic speck of silver catalyst and reducing silver located at another site, this being easily possible on account of the high electrical conductivity of the metallic mass of the catalyst."

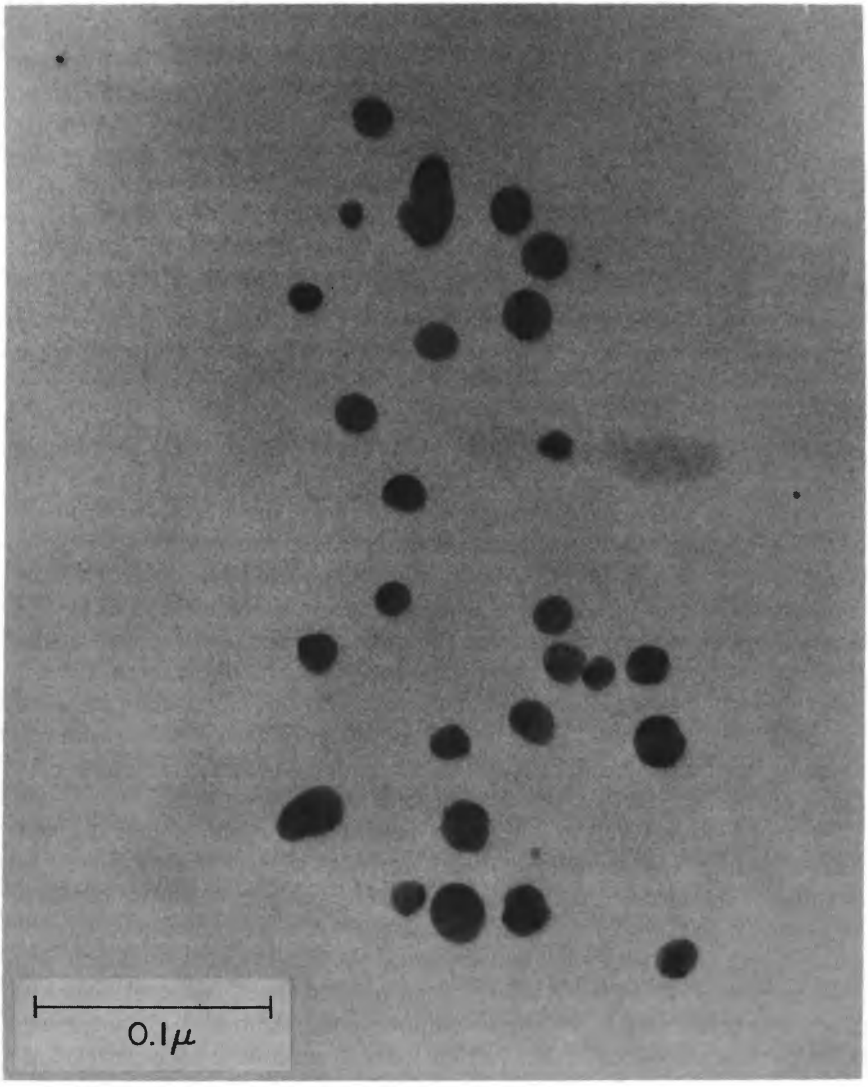


Figure 8. Electron micrograph of the silver produced in the initial stages of development before filament formation begins. [J. F. Hamilton, *App. Opt.*, 11: 16 (1972)]

Regardless of the exact mechanism—and both possibilities may occur at different stages of the growth of the latent image—an atom of silver is added at the latent image site when the electron interacts with the silver ion from the crystal. The silver atoms should be added around the periphery of the latent image (catalysis theory) or at the underside of the latent image (electrode theory). The very first silver atoms added do appear to enter the latent image near its periphery, flowing over the surface to maintain a compact spherical structure.[95] Later, when filament formation occurs, the electrode theory appears to offer the simplest mechanism of silver growth. Silver atoms are formed at the underside of the latent image speck; and when their rate of accumulation is sufficient, the filament of silver is extruded from the crystal by the pressure of the silver atoms accumulating at the base. Thus, initiation and then continuation of development might be explained by two different mechanisms.[96]

During the formation of the filament silver at the latent image site, mobile silver ions move through the silver halide crystal toward the base of the developing speck to replace the silver ions reduced to metallic silver. Bromide ions may be removed at a distance from the silver filament.[97,98] Recently, V. I. Saunders and W. West,[99] using single crystals of silver bromide, have shown that the flow of silver ions to the reduction site compensates for the excess bromide ions resulting from the reduction of the silver ions at the development center. Bromide ions do not appear to be liberated at this site but at the opposite face of the crystal where the bromide ions are in excess of the available silver ions. The bromide ions leave the face of the crystal opposite to the face where the silver filament is being produced. Pits are produced on the face where the bromide ions leave the crystal. E. Klein and R. Matejec[97] found etch pits near the development center, indicating that the nearby silver ions were being used to form the silver filaments. The silver bromide crystal face containing alternating silver and bromide ions has been suggested[100] to be a favorable arrangement for the bromide ion to go into solution and the silver ions to move toward the development center.

As early as 1949 Alfred Kuster[101] had noticed that "Different chemical developers containing Metol, hydroquinone, rodinal, amidol, glycine, pyrogallol, pyrocatechol, and ferrous oxalate in the usual combination as developing agents, produce silver grains which hardly differ from each other under electron microscopic radiation; in some cases unimportant differences were found in the width of the ribbon of silver threads."

In the absence of physical development, filaments of silver produced by development of various emulsion compositions with various developers are approximately 200 Å in diameter. This uniform diameter formed under varied conditions suggests that some property of silver, but not of the silver halide or the developer used to produce the silver, is the determining factor

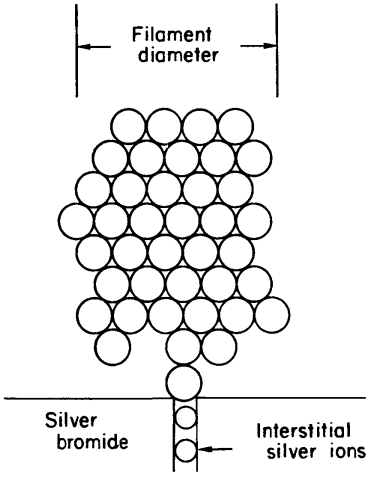


Figure 9. Elementary silver forming at a silver bromide surface. Direct development in a low-solvent solution often forms filamentary silver with a diameter of about 200 Å. These filaments, about 70 atoms wide, form when the initial spherical silver particle grows too large for the silver atoms to diffuse over the whole sphere in the time available. [Chester R. Berry, *Phot. Sci. and Eng.*, 13: 65 (1969)]

in low-solvent developers. Chester R. Berry[102] has proposed that "the limiting factor is the surface diffusion coefficient for silver atoms on silver."

The first silver atoms at the start of development are formed at a point or in a very restricted area. Surface tension causes the atoms to pack themselves into a sphere, just like other colloidal silver particles formed by other methods. However, when the sphere reaches a certain size, the newly formed silver atoms do not have sufficient time to move completely around it; the result is an elongation. New layers of silver atoms are formed, and these push the elongated mass of atoms away before the new atoms can migrate completely around the sphere. (See Figure 9.)

The competition for available silver atoms for either expanding the diameter of the original sphere or expanding the length of the filament results in a filament when the sphere's radius reaches a critical value. This critical value, the diameter of the silver filament, has been measured to be around 200 Å, or about 70 atoms of silver wide.

SUBSEQUENT REACTIONS OF THE DEVELOPING AGENT

The loss of one electron by a molecule of the developing agent produces a semiquinone, a free radical, whose low stability impels it to change to a more stable electronic form. The semiquinone of hydroquinone has less stability than the semiquinone of Phenidone, so that the reactivity of the hydroquinone intermediate is greater than that of the intermediate of Phenidone. In addition, the composition of the developing solution may influence the

further reactions of the developing agent. These are the possible reactions that may occur:

1. The semiquinone of the developing agent may give up a second electron to the latent image. The oxidized form of the developing agent would then desorb and go into the surrounding solution.
2. Two semiquinones may react with each other, forming one molecule of the developing agent that is the reduced form and another molecule that is completely oxidized (two electrons lost). It is possible that the oxidized form may interact with the reduced form, yielding two intermediate semiquinones, such as hydroquinone interacting with quinone to form two semiquinones.
3. In the presence of sodium sulfite in the developing solution, the reactions of the oxidized and reduced forms of the developing agent may not occur. The primary reaction is between the oxidized form of the developing agent and the sulfite to form the monosulfonate of the original developing agent. This reaction can occur with the benzenoid developing agents but not with Phenidone or L-ascorbic acid. Phenidone, for example, upon losing one electron, gives an intermediate form that dismutates, producing one molecule of Phenidone and one molecule of a pyrazolone, the final oxidation product, when two molecules of the intermediate react.
4. The semiquinone of an adsorbed developing agent may be regenerated to its original form by the donation of an electron from a secondary developing agent of the developing solution. The semiquinone of the secondary developing agent may then react with sulfite, as in (3), or interact with other molecules of the same compound, as in (2).

The presence of a primary and a secondary developing agent in the same developing solution produces a cooperative action in which the developed silver is greater than the sum of the silver produced by the agents used individually. This enhancement of development is called superadditivity of development.[103,104] For superadditivity to occur, the primary developing agent should be strongly adsorbed and have a relatively stable semiquinone after the one electron transfer. Regeneration of this adsorbed semiquinone should almost be complete by the secondary developing agent for maximum cooperative action to occur. In addition, the semiquinone of the primary developing agent should be neutral or positively charged, as a negatively charged semiquinone may repel the approach of the negatively charged ion of the secondary developing agent.[105–113]

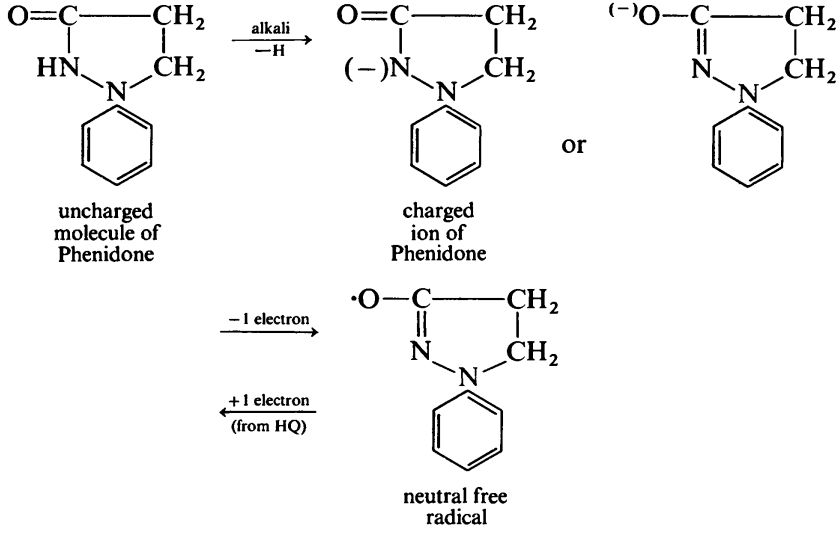
Most modern developers use two superadditive developing agents. The superadditive combination of Metol with hydroquinone was used almost exclusively for many years.[114] The regeneration of Metol, the primary

developing agent, by hydroquinone was suggested by Gerald I. P. Levenson[104] to occur in the following manner:

1. Metol − 1 electron ⟶ oxidized Metol (methylquinoneimine).
2. Oxidized Metol + sodium sulfite $\xrightarrow{\text{slow}}$ Metol monosulfonate.
3. Oxidized Metol + hydroquinone $\xrightarrow{\text{fast}}$ Metol + quinone.
4. Quinone + sodium sulfite $\xrightarrow{\text{fast}}$ hydroquinone monosulfonate.

In this reaction scheme, Metol is the primary developing agent and hydroquinone is thought to act chiefly to regenerate the Metol from its one-electron-lost form. Levenson was able to compound Metol-hydroquinone developers below pH 9.2 in which the hydroquinone would be oxidized only when Elon was present. At this pH the hydroquinone was incapable of reacting with silver ions but could react with the very active semiquinone of Metol.

Many of the modern developing solutions contain hydroquinone and Phenidone as superadditive developing agents.[115] In alkaline solution Phenidone is thought to ionize, then transfer one electron:



This formation of an uncharged free radical when ionized Phenidone lost one electron was proposed by A. J. Axford and J. D. Kendall[116] and later supported by the work of S. Horrobin, D. W. Ramsay, and L. F. A. Mason.[117] The oxidation of Phenidone has been studied extensively.[118–122] Aminopyrazolines showed superadditive effects with hydroquinone and pyrogallol but not with Metol, Amidol, or 3-pyrazolidones.[123]

Many developing agents form superadditive developers with hydroquinone. It was concluded by J. F. Willems and G. F. van Veelen[124] that for maximum superadditivity to occur, the primary developing agent must be as active as possible, the semiquinone must form easily and be relatively stable, and the semiquinone must be neutral or positively charged. If the semiquinone contains a negatively charged group, superadditivity is low with hydroquinone even though the primary developing agent may be an active compound with a stable semiquinone. As these investigators point out, "The semiquinones also play a prominent part in minimizing the unfavorable effect of negative charge barrier around the silver halides, thereby facilitating the access of the hydroquinone anions either directly to the silver halide or to the adsorbed semiquinone itself." Almost all semiquinones that are efficient in superadditive combinations are uncharged, except those of *p*-phenylenediamine, which are positively charged.

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Chapter 7
Photographic Solutions

There is nothing mysterious in the art of mixing solutions for photographic processes which requires previous knowledge of voodoo, transcendentalism, or chemistry, but observation of a few simple rules makes the job easier and safer.

ALLEN R. GREENLEAF[15]

Photographic processing involves the treatment of photosensitive materials with one or more chemical compositions. The latent image of black-and-white photographic films and papers is amplified by development, the amplification being stopped at the optimum point by a stop bath, and the unused silver salts are solubilized during fixation. These chemical actions may be carried out in a combined developer-fixer (monobath). The light-stopping ability of the metallic silver image can be increased by intensification or lessened by reduction; the color of the silver image may be changed by toning. Processing of color photographic materials involves a number of chemical operations—hardening, dye formation, clearing, bleaching, and stabilizing—besides silver development and fixation. Even from this incomplete listing of photographic treatments it is evident that chemical reactions make photography possible.

Most chemical compounds are solids. Silver salts and the metallic silver image are solids that are embedded in another solid, the gelatin of the emulsion layer. Solid chemicals cannot penetrate the gelatin layer but some

liquids, especially water, can. When water diffuses into gelatin, the water causes the gelatin to swell, making passage more easy through the gelatin. Dissolving the solid chemicals in the water allows the chemical compounds to diffuse into the gelatin and react with the solids immobilized in the swollen gelatin layer. Most chemicals are more reactive when dissolved in water, so that water serves as a carrier of the chemicals as well as providing a medium for the chemical reactions to occur. Dispersion of the crystalline solid chemical in the water, or another liquid, produces a solution that contains the particles of the chemical evenly distributed throughout its volume. Several compounds can be dissolved in water to form a chemically balanced processing bath.

Photographic solutions are mixtures of one or more solids, liquids, or gases in a liquid. The substance being dissolved is called the solute; the liquid in which the solute is dissolved is called the solvent. The maximum quantity of solute that will dissolve in the solvent is the limit of its solubility, producing a saturated solution. The solubility of a compound depends upon the temperature and the kind of solvent. Each compound has its own characteristic solubility in each solvent. Sometimes it is desirable to add the solid compound to one solvent, such as methyl alcohol, in which the compound is readily soluble, before adding it to the water solution, in which the compound alone dissolves only with difficulty. A heated solution will dissolve more solute than a cold solution, so mild heating is often used to insure the rapid and complete solution of photographic chemicals. If the solution was saturated at the higher temperature, crystals of the solute will settle out when the solution is cooled until the limit of solubility at the lower temperature is reached. At the point of saturation the particles of the compound being dissolved are equal to the number of particles that are being deposited as a solid. Adding more solute to a saturated solution only increases the quantity of the undissolved substance. Some of the dissolved compound separating out from a saturated solution may associate with some of the molecules of the solvent. In the case of water as the solvent, these associated molecules of water in the crystalline compound are called the water of crystallization.

The particles or molecules of a photographic chemical occupy a certain space in solution, so that the volume of the solution is usually greater than the volume of the solvent alone. The same weight of two different compounds do not necessarily cause equal increases in volume. Mixing two liquids may yield a solution that is less than, equal to, or greater than the sum of the volumes of the two liquids. For example, mixing one volume of methyl alcohol with one volume of water gives a volume that is less than the sum of their two volumes.

Gases such as ammonia or formaldehyde may be dissolved in water to produce ammonium hydroxide, which is a saturated solution containing

about 29% of ammonia, or formalin, which is about 40% formaldehyde. Solutions containing dissolved gases are not stable in composition, as the gas escapes continuously from the water solution. Evolution of the gas is increased if the solution is warmed or the atmospheric pressure is decreased—for example, during in-flight processing.

The making of photographic solutions involves first the measurement of each ingredient by weight or volume and then the dissolution of each in a volume of solvent. Photographic manufacturers often provide convenience by weighing and packaging photographic chemicals so that the user need only dissolve the single blended mixture or a few separate mixtures to make a processing bath. Some photographic compositions are supplied already in solution, although most of these are in concentrated form that requires dilution with water before use. The making of photographic solutions requires a knowledge of the units of measurement so that the solutions can be made precisely and accurately each time they are needed.

SYSTEMS OF MEASUREMENT

Ever since ancient man began to communicate with his fellows, there has been a need for standards of measurement. Early measures were based on physical dimensions; for example, the Egyptian cubit was the distance from the end of a man's finger to his elbow. An inch was the width of a man's thumb, a hand was four inches, a foot was the length of a man's foot (reputedly, the foot of Charlemagne), and the yard was the distance from the end of the nose of England's King Henry I to the end of the thumb of his outstretched arm. Measures of volume and weight were often based on the physical dimensions of containers and objects. Unfortunately, each nation devised its own systems of measurement, and sometimes several similar systems were used for essentially the same purpose. Competing systems were often only difficultly interchangeable among each other or with the measures of other nations.

Virtually all measurements needed in our present world can be derived from the four, and only four, independent units for length, mass, time, and temperature.[1] The modern need for scientific communication and the interchangeability of industrial products in world trade has caused the international acceptance of standard units for these four quantities as defined by the International System of Units (Système International, or S. I.; see Table 1).[2] Almost every nation on Earth, with the primary exception of the United States, has changed, or is in the process of changing, to this system of international measures. Currently, the United States is studying such a

Table 1. International System of Units (S. I.)

Division of Unit	Multiples and Submultiples	Prefixes	Symbols
One trillion times	1 000 000 000 000 = 10^{12}	tera (ter'a)	T
One billion times	1 000 000 000 = 10^{9}	giga (ji'ga)	G
One million times	1 000 000 = 10^{6}	mega (meg'a)	M
One ten thousand times	10 000 = 10^{4}	myria (myr'i·a)	my
One thousand times	1 000 = 10^{3}	kilo (kil'o)	k
One hundred times	100 = 10^{2}	hecto (hek'to)	h
Ten times	10 = 10^{1}	deka (dek'a)	da
One time	1 = 10^{0}	(standard unit)	m, g, l*
One tenth of unit	0.1 = 10^{-1}	deci (des'i)	d
One hundredth of unit	0.01 = 10^{-2}	centi (sen'ti)	c
One thousandth of unit	0.001 = 10^{-3}	milli (mil'i)	m
One millionth of unit	0.000 001 = 10^{-6}	micro (mi'kro)	μ†
One billionth of unit	0.000 000 001 = 10^{-9}	nano (nan'o)	n
One trillionth of unit	0.000 000 000 001 = 10^{-12}	pico (pe'ko)	p

* A standard unit is a meter (m), gram (g), or liter (l).
† One millionth of a meter is called a micron.

change, too, but the enormous cost to this industrialized nation will make such a conversion slow in coming.

The meter for length, the kilogram for mass, the second for time, and the degree Celsius (or kelvin; kelvin = degree Celsius) for temperature are the international standards. These new standards are based on the metric system, a decimal system first established in France in 1801. The basic unit of the metric system, the meter (or metre), was first defined as one ten-millionth of the distance covered by a certain quadrant of the Earth from the Equator to the North Pole. The mass of water at its maximum density of a cube measuring one-tenth meter on a side was defined as a kilogram of weight. The volume or capacity of this cube was called a liter (or litre). The degree Celsius is equivalent to the degree centigrade as a measure of temperature, with water freezing at zero degrees and boiling at 100 degrees.

Modern definitions of these original standards have been established, and these new precise standards are now part of the S. I. units. These standards of measurement are particularly useful for preparing photographic solutions and carrying out photographic processing. S. I. units will be used in this book, but some photographic formulations and instructions may be given in the original units specified.

All S. I. units are related decimally. Latin prefixes indicate decimal divisions of the unit; Greek prefixes indicate multiples of the unit. These prefixes are combined with the word for the basic unit (meter, gram, or liter) to produce the name for multiples or divisions of the basic unit. (See Table 1.)

One thousandth (0.001) of a liter is a milliliter and one thousandth of a gram is a milligram. One thousand grams are a kilogram. In photographic practice, milligrams, grams, and kilograms are the usual measures of weight, and milliliters and liters are the usual measures of capacity. The other units are seldom used for compounding photographic processing solutions. Each liter (l) has 1000 milliliters (ml). Each liter contains water that weighs one kilogram (kg) under standard conditions. Thus, each milliliter of water weighs one gram (g). The cubic centimeter (cm^3), the metric measure of volume, is often used interchangeably with the milliliter, although 1 ml = 1.000028 cm^3. In the older formulations for photographic solutions, the cubic centimeter was often abbreviated as cc.[3] For photographic purposes cubic centimeters and milliliters may be considered to be equivalent.

The formulas for many photographic solutions, especially those compounded in Great Britain or the United States, are often stated in terms of avoirdupois weights, such as grains, ounces, or pounds, and in liquid measures of fluid ounces, quarts, and gallons. Eventually, these formulations will be expressed in S. I. units, but until then the maker of photographic solutions may have to make his own conversions. This may be done by using the conversion tables (Table 2). It should be noted that British measures may differ from the U. S. units of the same name. For example, the British Imperial gallon (4.546 liters) is larger than the U. S. gallon (3.785 liters) by 20%.[4]

MATERIALS FOR MIXING SOLUTIONS

The necessary ingredients for making a photographic processing solution are photographic chemicals and water. Both should be as pure as possible, because impurities distribute evenly through the solution and may produce competitive but unwanted chemical reactions.[5] The chief ingredient in a photographic solution is water. Distilled water, if available, is to be preferred, particularly for fine-grain developing solutions and intensifying solutions. Most alkaline developers and reducing solutions need reasonably pure water that is free from foreign matter. Fixing baths can be prepared with most water, but toning solutions usually require the purest water available. Even the hardness in water may interfere. Boiling tap water for 20 minutes will destroy temporary water hardness due to bicarbonate salts and drive off absorbed gases. Filtering the boiled water will remove the insoluble matter.

Table 2. Weights and Measures—Conversion Tables[4]

Avoirdupois to Metric Weight

Pounds	Ounces	Grains	Grams	Kilograms
1.0	16.0	7000.0	453.6	0.4536
0.0625	1.0	437.5	28.35	0.02835
		1.0	0.0648	
	0.03527	15.43	1.0	0.001
2.205	35.27	15430.0	1000.0	1.0

U.S. Liquid to Metric Measure

Gallons	Quarts	Fluid Ounces	Fluid Drams	Cubic Centimeters	Liters
1.0	4.0	128.0	1024.0	3785.0	3.785
0.25	1.0	32.0	256.0	946.3	0.9463
		1.0	8.0	29.57	0.02957
0.000975	0.0039	0.125	1.0 (60 mins.)	3.697	0.003697
		0.03381	0.2705	1.0	0.001
0.2642	1.057	33.81	270.5	1000.0	1.0

Solid Conversion Values

Grains per 32 ounces multiplied by	0.06847	= grams per liter
Ounces per 32 ounces multiplied by	29.96	= grams per liter
Pounds per 32 ounces multiplied by	479.3	= grams per liter
Grams per liter multiplied by	14.6	= grains per 32 ounces
Grams per liter multiplied by	0.03338	= ounces per 32 ounces
Grams per liter multiplied by	0.002086	= pounds per 32 ounces

Liquid Conversion Values
(U.S. System)

Ounces (fluid) per 32 ounces multiplied by	31.25	= cubic centimeters per liter
Cubic centimeters per liter multiplied by	0.3200	= ounces (fluid) per 32 ounces

Table 2. (*continued*)

British Imperial Liquid to Metric Measure

Gallons	Quarts	Fluid Ounces	Fluid Drams	Cubic Centimeters	Liters
1.0	4.0	160.0	1280.0	4546.0	4.546
0.25	1.0	40.0	320.0	1136.0	1.136
		1.0	8.0	28.41	0.02841
	0.003125	0.125	1.0 (60 min.)	3.551	0.003551
		0.03520	0.2816	1.0	0.001
0.2200	0.8800	35.20	281.6	1000.0	1.0

Solid Conversion Values

Grains / Ounces / Pounds } per British imperial quart (40 fluid ounces) multiplied by 0.833 = grains / ounces / pounds } per U. S. quart (32 fluid ounces)

Grains per British imperial quart multiplied by 0.05696 = grams per liter

Ounces per British imperial quart multiplied by 24.92 = grams per liter

Pounds per British imperial quart multiplied by 398.7 = grams per liter

Grams per liter multiplied by 17.54 = grains per British imperial quart

Grams per liter multiplied by 0.0401 = ounces per British imperial quart

Grams per liter multiplied by 0.002506 = pounds per British imperial quart

Liquid Conversion Values

Ounces (fluid) per British imperial quart multiplied by 0.8 = ounces (fluid) per U. S. quart

Ounces (fluid) per British imperial quart multiplied by 25.00 = cubic centimeters per liter

Cubic centimeters per liter multiplied by 0.03999 = ounces (fluid) per British imperial quart

Most photographic chemicals are in good condition when first purchased in sealed containers. The best possible quality of developing agents is to be preferred because of the importance of these compounds in image formation. It is advisable to date each container of developing agents and other photographic chemicals when purchased. When fresh, most developing agents are white or colorless, but in moist air they begin to oxidize, a process usually

Table 3. Common Photographic Chemicals: Effect on Skin, Paper, and Cloth; Appearance after Exposure and Deterioration

Chemical	Color of Fresh Chemical	Appearance of Chemical after Exposure to Air			Effect of Chemical on	
		Slight Deterioration	More Advanced	Photographically Useless	Skin	Paper, Cloth
Amidol	White or bluish-gray	Gray specks	Gray	Black	Stains, toxic[a]	Black stains
p-Aminophenol hydrochloride	White	Light purple	Purple	Purple-black	Toxic	Black stains
L-Ascorbic acid	White	Light tan	Tan	Tan		Brown stains
Catechol	White	Gray	Gray-brown	Brown-black	Toxic, stains	Brown-black stains
Chlorohydro-quinone	White	Tan	Brown	Dark brown, caked		Green-brown stains
Glycin	White or gray	Tan	Brown	Dark brown		Green-brown stains
Hydroquinone	White	Brown specks	Light brown or green	Brown or green		Brown stains
Metol	White or yellowish-white	Brown or pink specks	Brown or purple	Black	Toxic	Brown stains

Phenidone	White	Pale pink	Pale pink	Tan		
p-Phenylenediamine dihydrochloride	White or grayish-white	Lavender	Purple	Black, caked	Toxic	Purple-brown stains
Pyrogallol	White	Grayish-tan	Brown	Black	Stains, toxic	Brown stains
Potassium carbonate	White	No visible change		Caked	Irritates	
Sodium carbonate monohydrate	White	No visible change		Caked	Irritates	
Trisodium phosphate·12H_2O	White	No visible change		Caked	Irritates	
Sodium hydroxide	White	Damp	Wet	Liquefied	Burns	Weakens paper, dissolves wool
Sodium sulfite (desiccated)	White	No visible change		Caked		
Sodium thiosulfate pentahydrate	White	Crystals lose water to form a powder		Amorphous white powder		Yellow stains

[a] The chemicals listed as "toxic" are those which produce a rash, or swelling, or other skin disorder on persons who are allergically sensitive to them.

indicated by color changes. Slight discoloration is not enough to make the compound unusable. Dark coloration (browns and blacks) indicates extensive oxidation; such chemicals should not be used. Strong alkalis, such as sodium and potassium hydroxide, if exposed to moist air, take up water and carbon dioxide, forming carbonates that are less alkaline than the hydroxides. If caked, alkaline materials should not be used because of their uncertain composition. Some compounds, such as sodium thiosulfate pentahydrate, may lose part of their water of crystallization, forming a powder that makes the thiosulfate compound of variable composition. Trisodium phosphate (TSP) normally has 12 molecules of water associated with each molecule of TSP. Upon standing, some of the water of crystallization may be lost, making it difficult to estimate the TSP content of the chemical. Deterioration in the less expensive chemicals, such as alkalis, sulfite, and thiosulfate, should cause these chemicals to be discarded, because their use would produce uncertain photographic results.

E. W. Lowe has prepared a table listing the effects of deterioration on common photographic chemicals, and the effect of these chemicals on human skin or on paper or cloth.[6] This table, slightly modified, is given here as an aid for evaluating the condition of photographic compounds. (See Table 3.)

MIXING SOLUTIONS OF KNOWN CONCENTRATION

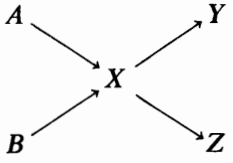
Percentage Solutions

When only a small amount of solute is contained in a solvent, the solution is said to be dilute; when a large amount of solute is present, the solution is concentrated. Word descriptions of the amount of solute present are not sufficient. A precise mathematical definition is necessary to distinguish the many possible variations of concentration. The percentage solution is often used to specify the amount of solute present.[7] For photographic purposes it is the practice to dissolve the percentage quantity in grams of a chemical in a volume of water less than 100 ml, then add sufficient water to make 100 ml. Five grams of sodium hydroxide may be added to 90 ml of water and, after the hydroxide is dissolved, water is added to give 100 ml of solution. This is a 5% photographic solution of sodium hydroxide, sometimes referred to as a 5% weight/volume (w/v) solution. There is 1 g of sodium hydroxide in every 20 ml of the 5% solution. Twenty milliliters of the solution will be required for every gram of sodium hydroxide that is in the formula. Surprisingly, it is possible to have photographic solutions of 100% or more with

very soluble compounds. One hundred grams of sodium thiosulfate does not occupy the volume of 100 ml, so this compound may be dissolved in sufficient water to make 100 ml of solution—a 100% solution of sodium thiosulfate.

Liquids may be used to make percent solutions. For example, a 10% photographic solution of a liquid may be made by measuring 10 ml of the liquid and adding sufficient water to make 100 ml. This is a 10% volume/volume (v/v) solution. Such a procedure may involve some approximation in the concentration of the chemical, because some of the liquids used in photographic practice are not pure but may contain a small percentage of water. Glacial acetic acid is commonly used to make acid stop baths. A 2% solution can be made by measuring out 2 ml of glacial acetic acid, adding this to 90 ml water, and then adding sufficient water to make 100 ml. Actually, glacial acetic acid is not 100% acetic acid but only about 99.5%. Thus, this 2% solution is not accurately 2% because of the presence of some water in the glacial acetic acid. This solution, however, is satisfactory for stop-bath use and is easily prepared in this fashion.

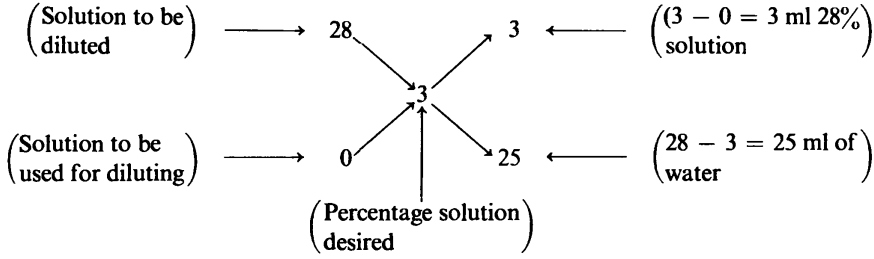
Sometimes it is required to prepare a percent solution from a percent solution of a higher value. Formulas often call for 28% acetic acid rather than glacial acetic acid. The 28% acetic acid is specified as there is less danger of violent reaction during mixing with the less concentrated acid. Assuming the glacial acetic acid to be 100%, 28 ml of the glacial acetic acid is added to about 50 ml of water, then sufficient water is added to make 100 ml of mixed solution (approximately 28% acetic acid). The above relationships of preparing percentage solutions may be stated in a general form for determining the quantities of two different solutions needed to give one solution of a desired percentage:[8]



Place at *A* the percent strength of the solution to be diluted,
B the percent strength of the solution used for diluting (if water, this value is zero),
X the percent strength of the desired solution,
Y the difference of subtracting *B* from *X*,
Z the difference of subtracting *X* from *A*.

Then add *Y* ml of *A* and *Z* ml of *B* to make *X*% solution.

This general relationship can be applied to the problem of making 3% acetic acid from 28% acetic acid.



A 3% acetic acid solution is made by adding 3 ml of 28% acetic acid to 25 ml of water, or a suitable multiple of these values to provide the desired solution volume.

It is quite possible with time that the human mind may forget the above relationships or become uncertain of the mathematical operations. The ever-present but forgetful human mind can always be used to solve percentage solution calculations. Each 100 ml of 28% acetic acid must contain 28 g of acetic acid, or 28/100 (0.28) g of the acid in each milliliter. If the problem is to make 500 ml of 3% acetic acid, then 15 g of acetic acid (3 g/100 ml times 5 equals 15 g of acid in 500 ml solution) is needed. Dividing the needed grams (15) of acid by the amount of acid in each ml (0.28 g) of the 28% acid yields the number of ml of the 28% acid required (53.6 ml). Adding the 53.6 ml of 28% acetic acid to 400 ml of water, and then adding sufficient water to make 500 ml of solution, will yield the desired 500 ml of 3% acetic acid.

Percentage solutions find wide usage in photographic processing. A small quantity of a chemical ingredient may be difficult to weigh accurately, but a few milliliters of a low-percent solution can provide the desired amount easily. A number of percent solutions of the basic ingredients of photographic formulas have been used to speed the mixing of a photographic solution such as a developer. The required volumes of each percent solution of the ingredients are measured and mixed together with sufficient water to make the desired volume of the solution.[9]

Molar Solutions

Sometimes it is desired to have solutions contain equal numbers of molecules rather than equal gram quantities. Each compound has a molecular weight, the sum of the atomic weights of the atoms composing the compound. The molecular weight expressed in grams is called the gram molecular weight.[10] The gram molecular weight of each compound contains the same number

of molecules, somewhat more than six hundred thousand million million million. A liter of solution containing one gram molecular weight of a solute is said to have one molar concentration of the solute, designated as a 1 *M* solution. Every 1 *M* solution contains the same number of molecules as every other 1 *M* solution. Every 0.0256 *M* solution has the same number of molecules as every other 0.0256 *M* solution.

Making molar solutions requires the knowledge of the molecular weight of photographic chemicals. Those of some common compounds used in photography are listed in Table 4.

Table 4. Molecular Weights of Photographic Chemicals

Photographic Chemical	Other Name	Molecular Weight
Developing Agents		
p-Aminophenol hydrochloride	*p*-Hydroxyaniline hydrochloride	145.59
Amidol	2,4-Diaminophenol dihydrochloride	197.07
L-Ascorbic acid		176.12
Catechol	*o*-Dihydroxybenzene	110.11
Chlorohydroquinone	2-Chloro-1,4-di-hydroxybenzene	144.56
Dimezone	4,4-Dimethyl-1-phenyl-3-pyrazolidone	190.18
Glycin	*p*-Hydroxyphenylaminoacetic acid	167.16
Hydroquinone	*p*-Dihydroxybenzene	110.11
Hydroxylamine hydrochloride		69.50
Metol (Elon)	*N*-Methyl-*p*-aminophenol sulfate	344.38
Phenidone	1-Phenyl-3-pyrazolidone	162.18
p-Phenylenediamine dihydrochloride	1,4-Diaminobenzene dihydrochloride	181.07
Pyrogallol	1,2,3-Benzenetriol	126.11
Alkalis		
Borax	Sodium borate ($10H_2O$)	381.42
Sodium carbonate		106.00

Table 4. *(continued)*

Photographic Chemical	Other Name	Molecular Weight
Sodium carbonate monohydrate		124.00
Sodium carbonate decahydrate		286.00
Sodium hydroxide	Caustic soda	40.01
Sodium metaborate		131.60
Sodium metaborate tetrahydrate		203.67
Sodium metaborate octahydrate		275.67
Potassium carbonate		138.20
Potassium carbonate $\cdot 1\frac{1}{2}H_2O$		165.20
Potassium hydroxide	Caustic potash	56.10
Trisodium phosphate dodecahydrate		380.16
Acids		
Acetic acid		60.05
L-Ascorbic acid		176.12
Boric acid		61.84
Citric acid $\cdot H_2O$		210.14
Sulfuric acid		98.08
Tartaric acid		150.09
Solvents		
Acetone		58.08
Benzyl alcohol		108.14
Diethanolamine	2,2′-Iminodiethanol	105.14
Ethyl acetate		88.10
Ethanolamine	2-Aminoethanol	61.08
Ethyl amine	Monoethylamine	45.08
Ethyl alcohol	Ethanol	46.07
Ethylenediamine	1,2-Diaminoethane	60.10
Ethylene glycol	1,2-Ethanediol	62.07

Table 4. *(continued)*

Photographic Chemical	Other Name	Molecular Weight
Glycerol (glycerine)	1,2,3-Propanetriol	92.09
Methyl alcohol	Methanol	32.04
2-Methylaminoethanol		75.11
Triethanolamine	2,2′,2″-Nitrilotriethanol	149.19
Triethylene glycol	2,2′-Ethylenedioxy-bis(ethanol)	150.17
Other Photographic Chemicals		
Ammonium thiocyanate		76.12
Ammonium thiosulfate		148.21
Benzotriazole		119.12
Ethylenedinitrilotetraacetic acid tetrasodium salt		380.17
Glutaraldehyde		100.12
5-Methylbenzotriazole		133.15
1-Phenyl-2-tetrazoline-5-thione		178.20
Potassium bromide		119.01
Potassium chloride		74.55
Potassium dichromate	Potassium bichromate	294.21
Potassium ferricyanide		329.25
Potassium iodide		166.03
Potassium metabisulfite		222.32
Sodium bisulfite		104.07
Sodium chloride		58.45
Sodium formaldehyde bisulfite		134.09
Sodium persulfate	Sodium peroxydisulfate	238.10
Sodium sulfate		142.06
Sodium sulfate decahydrate		322.06
Sodium sulfite		126.06
Sodium sulfite · $7H_2O$		252.16
Sodium thiocyanate		81.08
Sodium thiosulfate		158.13
Sodium thiosulfate · $5H_2O$		248.18
Thiourea		76.12

MIXING SOLUTIONS FROM FORMULA

Published formulas of photographic solutions contain both the order of mixing and the quantity of chemicals to be used. The order of mixing is of importance, as some chemicals, such as Metol, will precipitate from water solutions that already contain other chemicals, such as sodium sulfite, of the formulation. Other compounds (Glycin, for example) are not very soluble in water but are much more readily dissolved if the water contains the sodium sulfite first. Dissolve each chemical in order of listing before adding the next compound to the solution.

The first ingredient of most photographic formulas is a volume of water, usually one-half or three-quarters of the total volume of the final solution. If the written formula starts with a solid compound as the first ingredient, it is the usual practice to take about three-quarters of the final volume of water stated in the last line of the formulation. The temperature of the water is often stated; if not, water at room temperature is assumed. The temperature of the water should not be any higher than necessary, as higher temperatures promote oxidation of the ingredients. Most formulas specify the final solution volume in the last line as "water to make." However, some prepared chemical mixtures are added to a specified volume of water and no further water is added. Photographic formulas may make a concentrated solution, called a stock solution, that is to be diluted with water or other concentrated solutions just before use.

Photographic developing solutions should be made most carefully, as even minor variations from the written formula may cause significant changes in the developed image. An example of a written formula is that of Kodak Developer D-76:

Kodak D-76 Developer

Order of Addition	Purpose of Ingredient	Name of Ingredient	Quantity
1	Solvent	Water, about 125°F (50°C)	750 ml
2	Developing agent	Kodak Elon developing agent	2 g
3	Preservative	Sodium sulfite, desiccated	100 g
4	Developing agent	Hydroquinone	5 g
5	Alkali	Borax, granular	2 g
6	Solvent	Water to make	1 liter

Each ingredient of the formula is added slowly to the water and the solution stirred until solution is complete. In some formulations with difficultly soluble developing agents the addition of the alkali may be necessary before solution can be achieved. Mixed developers should be stored in clean containers, preferably glass bottles. If a considerable volume of developing solution is prepared at one time, it is preferable to store the solution in several small bottles.[11] Storage in a single large bottle usually results in a large air space above the solution after some developer is used. The oxygen in the air causes the developing agent to oxidize and limits the life of the stored developer.

Some common chemicals used for mixing photographic solutions are available in different forms depending upon the amount of water associated with the compound.[12] No water of crystallization is present in the anhydrous or desiccated form, although the desiccated form may have been made by a slightly different manufacturing procedure than the anhydrous form. Anhydrous and desiccated forms of the same compound are interchangeable. Compounds may occur in one or more crystalline forms in which definite numbers of water molecules are associated with the compound. Sodium carbonate, sodium sulfite, sodium sulfate, and sodium thiosulfate are commonly used photographic chemicals that are available in anhydrous (desiccated) or crystalline form. Sodium carbonate, for example, may be specified in a formula as anhydrous (Na_2CO_3), as a monohydrate ($Na_2CO_3 \cdot H_2O$), or as crystals ($Na_2CO_3 \cdot 10H_2O$).

The anhydrous and crystalline forms of the same compound are interchangeable but not with equal gram quantities. More of the compound is required when water of crystallization is present than with the anhydrous form. Sodium carbonate is a common source of alkali in photographic developers. The anhydrous (desiccated) form of sodium carbonate should be free of water but, under practical conditions, usually contains up to 2% water gained during manufacture.[13] Once the container has been opened, the compound will tend to gain moisture from the air until about 15% is water. The exact quantity of water present is uncertain, and this may lead to variable alkalinity in different mixings from the same formula. The anhydrous carbonate stops gaining water when the water content is 15%, forming a stable monohydrated form. The monohydrate of sodium carbonate is manufactured, and this stable form is commonly specified in today's formulations. Crystal carbonate, containing 63% water or 10 molecules of water, has also been available and may be specified in photographic formulas. Upon exposure to air, the $Na_2CO_3 \cdot 10H_2O$ tends to lose water slowly until nine molecules have left, forming the stable monohydrate form. There is a possibility of variation in the alkalinity of crystal carbonate unless the history of the carbonate is known and compensation made for any change in

its composition. Because of the instability of both the anhydrous and decahydrate forms, sodium carbonate monohydrate is the preferred photographic form.

The truly anhydrous and hydrated forms of a photographic chemical are interchangeable if compensation is made for any water that is present. If the hydrated form is specified in a formula, and anhydrous is available, then a lesser quantity of the water-free compound is needed. If crystal sodium carbonate is specified, 57% less of the monohydrated form is needed; if anhydrous is specified, 17% more of the monohydrated is needed. The relationships between anhydrous and hydrated forms of four commonly used photographic chemicals are as follows:

Compound	Anhydrous or Desiccated	Monohydrated	Crystals
Sodium carbonate	1.0	1.17	2.7 ($10H_2O$)
Sodium sulfite	1.0		2.0 ($7H_2O$)
Sodium sulfate	1.0		2.3 ($10H_2O$)
Sodium thiosulfate	1.0		1.6 ($5H_2O$)

Energy must be supplied before a crystalline hydrate can be disrupted so that it can be dissolved in water.[14] This energy is supplied from the heat of the water, causing the solution to cool during dissolution. When considerable quantities of a crystalline hydrate are used, such as the crystals of sodium carbonate, sodium sulfite, or sodium thiosulfate, the cooling effect is striking and may crack glass bottles. During manufacture heat must be supplied to produce an anhydrous form of the carbonate, sulfite, or thiosulfate. When the anhydrous forms of these compounds are dissolved in water, this heat is evolved, causing the solution temperature to rise. Warm water is generally used for making solutions with crystalline hydrates, particularly sodium thiosulfate pentahydrate, and cool water for anhydrous compounds such as the anhydrous sodium thiosulfate.

The addition of a strong acid or base may cause a considerable heating effect when these compounds are dissolved in water. Sodium hydroxide or potassium hydroxide, or sulfuric acid, are common photographic chemicals whose dissolution in water may cause spattering of the solution. A small amount of a strong acid or base should always be added slowly to a considerable volume of water. The reverse order of this addition, adding the water to the acid or base, may release so much heat that the first few drops of water may be heated to boiling, thus causing a dangerous spattering of the solution, which is still strongly acidic or basic. Allen R. Greenleaf[15] notes

that "loss of eyesight or permanent disfigurement or both is a common result of this form of carelessness." Glass containers may shatter as a result of the sharp rise in temperature of the solution. Protective safety glasses should be worn during the mixing of these photographic solutions. The correct order of addition, acid or base slowly to the water, minimizes the danger. In addition, it is wise to start with cool water.

Sometimes a photographic chemical may be replaced by another compound of similar properties. Such a replacement, in some cases, is only approximate. Hans Windisch[16] listed the ratios of the following equivalent amounts of substituted chemicals:

Crystal sodium sulfite to potassium metabisulfite	as	2:0.9
Anhydrous sodium bisulfite to potassium metabisulfite		1:1
Anhydrous sodium carbonate to potassium carbonate		1:1.3
Crystal sodium carbonate to potassium carbonate		2:1
Sodium hydroxide to potassium hydroxide		1:1.4
Sodium hydroxide to crystal sodium carbonate		1:12
Sodium hydroxide to anhydrous sodium carbonate		1:4.5
Sodium hydroxide to potassium carbonate		1:6
Sodium hydroxide to tribasic sodium phosphate		1:5

Great care should be used in substituting one alkali for another, as differences may occur in many cases. More than alkalinity may be involved. For example, trisodium phosphate cannot be substituted for sodium carbonate if the developing agent, *p*-aminophenol, is in the solution. *p*-Aminophenol is precipitated in the presence of the trisodium phosphate. Potassium salts often produce a different reactivity than the corresponding sodium salts. Borates react with *o*-dihydroxy developing agents, such as catechol. There is no substitute for hydroxides when very high alkalinity is necessary.

MIXING A SOLUTION FROM "PARTS"

Photographic formulations may be stated in "parts." Parts should be taken to mean units of volume for liquids and as units of weight for solid ingredients. A part may be any unit of volume or weight (avoirdupois, metric, or other system), but all part quantities must be reckoned in the same units of volume or weight.[17] If the metric units are used, 10 parts of sodium sulfite to be added to 100 parts of water may mean to add 10 g of sodium sulfite to 100 ml (or 100 g) of water. In the preparation of an alcohol solution, the directions may state to use one part methanol and five parts water. Whatever volume is taken

for the methanol, then five times that volume of water should be used: 1 ml of methanol and 5 ml of water or one liter of methanol and five liters of water both satisfy the directions. The volume of the one part of methanol is taken such that the final volume (one part + five parts) is of sufficient quantity for the desired use.

Consider the formula and directions for use of the universal paper developer called Kodak D-72 Elon-Hydroquinone Developer. This formula is suitable not only for the development of photographic papers but also for lantern slides and as a rapid developer for press negatives.

Kodak D-72 Developer: Stock Solution

Order of Addition	Purpose of Ingredient	Name of Ingredient	Quantity
1	Solvent	Water (125°F or 52°C)	500 ml
2	Developing agent	Metol (Elon)	3 g
3	Preservative	Sodium sulfite (desiccated)	45 g
4	Developing agent	Hydroquinone	12 g
5	Alkali	Sodium carbonate, monohydrated	80 g
6	Restrainer	Potassium bromide	2 g
7	Add cool water to make		1 liter

Dissolve chemical ingredients in the order specified. Directions for the use of this developer are given in the *Photo-Lab Index*:[18]

For use with Kodak Azo, Illustrator's Azo, Ad-Type, Velox Rapid, Kodabromide and Resisto Rapid—dilute 1 part stock solution, 1 part water, and develop 1 minute at 68°F (20°C). For warmer tones on Kodabromide, dilute 1:3 or 1:4 and $\frac{1}{4}$ oz. (8 cc) 10% potassium bromide for each 32 oz. (1.0 liter) of working solution, and develop $1\frac{1}{2}$ minutes.

For Lantern Slides dilute 1:2. Develop 1 to 2 minutes at 68°F (20°C). For greater contrast dilute 1:1 and for less contrast 1:4.

For Press Negatives dilute 1:1. Develop about 5 minutes without agitation or 4 minutes with agitation for average contrast at 68°F (20°C). For less contrast dilute 1:2. For greater contrast, use full strength. Greater or less contrast may be obtained also by developing longer or shorter times than those indicated.

For Kodabromide paper, the directions specify one part stock solution and one part water. If one liter of solution is needed for processing the photographic prints, then 500 ml (one part) of the stock solution is added to 500 ml (one part) of water. For warmer tones on this paper, the directions specify a 1:3 or 1:4 dilution with 8 ml of 10% potassium bromide added to each liter of the working solution. For the 1:3 dilution, take 250 ml (one part) of the stock solution and add it to 750 ml (three parts) of water, then add the 8 ml of 10% potassium bromide. For the 1:4 dilution, take 200 ml (one part) of the stock solution and 800 ml (four parts) of water to make one liter of mixed solution, then add the 8 ml of 10% potassium bromide.

MIXING PHOTOGRAPHIC SOLUTIONS

Prepackaged dry photographic chemicals or concentrated liquids eliminate the need of a weighing device. For mixing a photographic solution from a formula, however, a scale or balance is required. The capacity of the balance is dependent upon the largest quantities that are routinely weighed. The sensitivity of the balance, or its accuracy, decreases as the balance is made more massive to handle heavier loads. Analytical accuracy is not needed for mixing photographic solutions; a balance sensitive to about 0.1 g is satisfactory for most preparations.[19] Chemicals should be weighed and solutions mixed in an area that is not part of the darkroom where photographic processing is done. This helps minimize chemical contamination of the processing area.

Small quantities of chemicals should be placed, not on the balance pan, but on a piece of paper on the pan. Weighing papers can be cut from almost any clean, dry paper, such as the onion skin paper used to prepare carbon copies of letters. The chemicals are transferred from the paper to the solution with a minimum of shaking of the paper; the paper is then discarded. Unnecessary shaking of the weighing paper can cause some of the chemical particles to float in the air, making the air possibly unhealthy to breathe, or the particles may later settle on photosensitive materials to cause spots. Shallow aluminum foil or plastic pans are also available for making weighings. Because the balance must be adjusted to compensate for the weight of the weighing paper or aluminum pan, it is desirable to have each paper or pan similar in weight to every other paper or pan. In some cases another piece of paper or pan can be used as a counterbalance. This reduces the time required to make successive weighings. Larger quantities of chemicals are usually weighed in metal scoops or pans. Because such containers must be used again and again, care should be taken to clean them so that chemical contamination is avoided.

Contamination of the human making the photographic solution should also be avoided. Safety glasses or a plastic safety shield should be worn over the eyes, one of the most vulnerable parts of the human body. Rubber gloves are recommended if strong alkalies and acids are used in volume. A protective laboratory apron is useful in avoiding chemical spotting of the clothing. Although the wearing of protective devices does decrease human efficiency, it is strongly recommended that the eyes be given protection during the measuring and mixing of liquids in the making of photographic solutions.

For measuring small volumes of liquids, graduated cylinders or graduated pipettes (calibrated tubes), usually of glass or plastic, are commonly used. The top of an aqueous solution, called the meniscus, will have a shallow dished appearance with the upper ends of the arc next to the inner surface of the graduate or pipette. The center level of the fluid should be even with the calibrated mark of the desired volume. The edges of the liquid are slightly higher, because capillary action pulls the liquid up the surface of the container. For very small volumes of a liquid, such as a milliliter or less, the pipette is used because of its greater accuracy. Pipettes can be filled much like soda straws but this is a dangerous technique when strong acids, alkalies, and other dangerous solutions are being measured. A bulb attached to the top end allows filling the pipette safely.

Solutions should be mixed in a container of adequate size to avoid splashing and overflow. Often glass beakers are used, but those larger than two liters are unwieldy and subject to breakage. Metal beakers, especially of stainless steel, are useful for making solutions up to four liters. Metal containers containing tin or lead should not be used, as these metals have a detrimental effect on photographic solutions. For volumes of four liters, or one gallon, larger stainless steel containers, such as buckets or tanks, are used. Generally, these have calibration marks representing units of volume, or can be calibrated individually, so that solutions can be brought to the final volume easily. Plastic containers are also finding increasing use as mixing vessels.

The rate of stirring, the kind and temperature of the solvent, which is usually water at temperatures ranging from room temperature to 125°F (52°C) but not higher, and the solubility and state of subdivision of solids are determining factors in securing homogeneous solutions. Continuous stirring is essential to secure rapid solution, but the rate should not be so vigorous as to draw air into the solution. A glass rod moved by hand is often sufficient to provide adequate agitation of small volumes of solution, but mechanical stirrers of the propeller type, or magnetic mixers with built-in heaters, are often necessary for mixing larger volumes of solution or dissolving difficultly soluble chemicals.

Solid pellets of sodium hydroxide will settle to the bottom of the mixing vessel and will not dissolve completely without vigorous agitation of the

surrounding liquid. Some anhydrous, finely divided chemicals will cake together if a considerable amount is added quickly to the solvent. Vigorous agitation will minimize this tendency. It is advisable to add any photographic chemical to the mixing vessel a little at a time to reduce the possibility of caking. Add the chemicals to the agitated solution, not the solvent to the dry chemical.

Increasing the temperature of the solvent hastens solution of photographic chemicals, but boiling water is not to be used. Water at such a high temperature would hasten oxidation of developing agents or decompose some chemicals into useless or detrimental products. Water at 125°F (52°C) is sufficiently warm to dissolve most photographic chemicals safely and quickly. When all the chemicals are dissolved in warm water, add cold water to bring the volume up to the desired level, then stir to insure the mixing of the complete volume. If this solution is to be used immediately, the solution may have to be cooled to reach the desired processing temperature.

Mixed solutions should be filtered before being used or stored. Photographic grade chemicals often contain foreign matter that is insoluble. Filtration through 120 grade cheese cloth, through cotton, through filter bags, through metal screens, or through filter paper will remove the insoluble extraneous matter from the mixed solution. If not removed, solid particles may adhere to the soft gelatin surface of photographic materials during processing. Filtration with filter bags or cheese cloth is adequate for several liters or less of solution. Automatic processing machines usually contain a filter of a pressure type in the line of the recirculation system so that both the fresh and replenished solutions are filtered continuously.

Mixed solutions should be stored in clean containers. Used bottles may be cleaned by filling them with hydrochloric acid diluted with an equal volume of water, then rinsing the bottle with water at least four times.[20] If the solution is subject to aerial oxidation, several smaller containers should be used rather than a single large one. Glass bottles are not altogether impervious to chemical attack but are the most satisfactory from the practical standpoint. Hard rubber containers absorb chemicals and later give them off to other solutions, and polyethylene plastic materials are permeable to the oxygen of the air. If a choice must be made, glass is to be preferred for storing all developing solutions, and plastic containers for fixing baths and other solutions less subject to changes in composition. Plastic containers should be clean and new or else should be used for the same kind of solution each time. Certain plastics absorb chemicals from the solutions stored in them. Reuse of a plastic container should be avoided if its previous history is unknown.

The alkalinity or acidity of a photographic solution has a strong influence on its activity. Measurement of this condition of a solution is difficult without suitable equipment. The pH of a solution may be estimated by using solutions

that change color with pH. These solutions are imbibed in paper strips, which are an inexpensive and simple means of estimating pH. By combining several dyes in the same solution or in the same paper strip, it is possible to observe color changes over a wide range of pH values.[21] One such wide-range pH indicator solution contained

Phenolphthalein	0.1 g
Methyl red	0.2 g
Dimethylaminoazobenzene	0.3 g
Bromthymol blue	0.4 g
Thymol blue	0.5 g
Ethyl alcohol	500.0 ml

Adding one drop of the above indicator solution to 1 ml of the photographic solution produced the following colors:

Color:	Red	Orange	Yellow	Green	Blue
pH:	2.0	4.0	6.0	8.0	10.0

For more accurate work the solution color should be compared with the colors of solutions of known pH value.

Rather than establish a colorimetric method, which requires considerable preparation, the common practice is to use pH-measuring instruments of greater versatility and greater cost. Rapid and accurate pH measurement requires the use of a battery-operated or plug-in pH meter, available in a wide range of sizes and kinds. Such meters are sensitive voltmeters with two electrodes that are dipped into the solution to be tested. One electrode provides a standard voltage, the other a voltage dependent upon the hydrogen-ion concentration of the test solution. The pH meter is so calibrated that the total voltage of the system is shown in pH values. G. I. P. Levenson[22] has listed the following approximate values of some common photographic solutions and other fluids. (See page 349.)

Measurement of solution temperature is often necessary while mixing or before using a solution. An accurate thermometer is essential; its accuracy should be checked before use. Some thermometers have both the Fahrenheit and Celsius (centigrade) temperature scales, but most have only one. Temperatures may be converted from one scale to the other by the following relationships[23,24]

$$(\text{degrees Fahrenheit minus } 32) \text{ times } \tfrac{5}{9} = \text{degrees Celsius}$$

$$(\text{degrees Celsius times } \tfrac{9}{5}) \text{ plus } 32 = \text{degrees Fahrenheit}$$

pH	Solution
14	4% (1 Normal) sodium hydroxide
13	0.4% Sodium hydroxide
12	Developers containing caustic alkali
11	Developers containing carbonate
10	
9	Fine-grain developers
8	Blood
7	Pure water; neutral solutions
6	Milk
5	Beer
4	Acid fixers and stop baths
3	Cider; orange juice; Coca-Cola
2	Lemon juice
1	Tenth normal sulphuric or hydrochloric acid
0	Normal solutions of strong acids

Water freezes at 32 degrees on the Fahrenheit scale but at 0 degrees on the Celsius (centigrade) scale. Thus, there are 32 Fahrenheit degrees difference between the two scales. Water boils at 100 degrees Celsius and 212 degrees Fahrenheit. Subtracting the 32 degrees difference from 212 gives 180 degrees; that is, 180 degrees Fahrenheit are equal to 100 degrees Celsius. Each Celsius degree is equal to 1.8 Fahrenheit degrees. (See Figure 1.)

To convert Fahrenheit degrees to Celsius degrees, first subtract 32, then divide by 1.8.

To convert Celsius degrees to Fahrenheit degrees, first multiply by 1.8, then add 32.

A common processing temperature is 68°F. This Fahrenheit temperature may be converted to Celsius by using the above relationship. Subtracting 32 from 68 gives 36. Dividing 36 by 1.8 gives 20, so that 68°F is equal to 20°C. Each increase of 1.8 deg above 68°F will produce a 1-deg increase in the corresponding Celsius temperature.

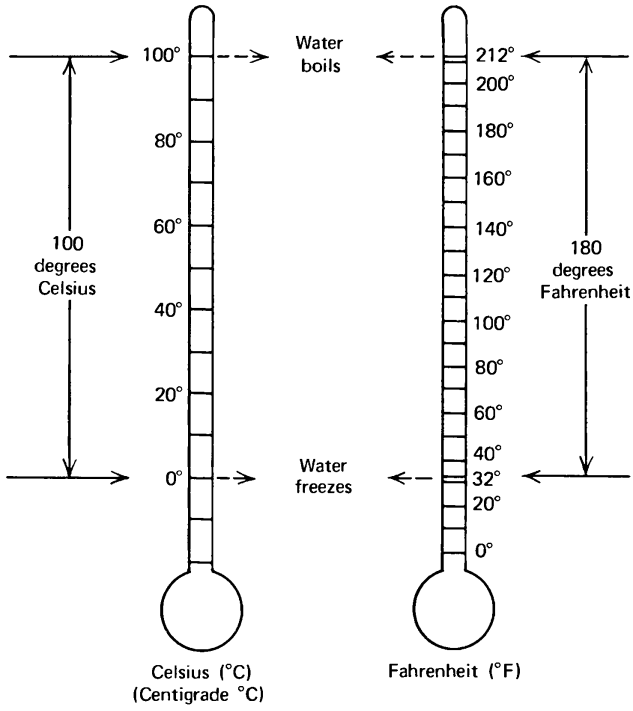


Figure 1. Celsius and Fahrenheit scales compared.

SAFE HANDLING OF PHOTOGRAPHIC PROCESSING CHEMICALS

J. B. Donaldson[25] has noted in the *Journal of the American Medical Association* that

The work of the photographer is frequently carried out under conditions inimical to health conservation. In part, these conditions are physical, represented by such items as darkness, the absence of sunlight, wetness, and abnormal air motion. Offensive odours, although in themselves innocuous, may serve so to limit the depth of breathing as to influence unfavourably the state of health. In addition, harm from specific chemical intoxicants is highly probable in photographic work. It is unlikely that any one photographer may daily be exposed to all the chemicals indicated on the lists shown of common photographic chemicals, although in the course of a month highly varied exposures might take place. As a result "mixed poisons" rather than specific agents are the likely causes of systemic diseases in photographers. However, metol, elon, chromium compounds, sodium carbonate, sulphur dioxide, and cyanides are known specific agents leading to localised injury among photographers.

As pointed out by Donaldson, the dangers to the photographer's health are far greater than usually imagined. Unsatisfactory working conditions are of increasing concern.[26] Geoffrey Crawley[27] has recently observed, "It is far better to be healthy and unemployed, than to be a millionaire on your death bed." Most of the concern for human health of those handling photographic materials has been related to specific chemicals, such as, for example, poisoning by formaldehyde,[28] thallium salts,[29] or chlorinated hydrocarbons (carbon tetrachloride).[30–32] As early as 1868 M. Carey Lea[33] was warning that "It is not that photography is necessarily a hurtful art, but its practice brings its votaries into contact with several very strong poisons which, if used without great care, and still more if used with the heedlessness that is only too common, are liable to produce the very worst effects. These substances are principally *ether, collodion, cyanide of potassium, corrosive sublimate, chloride of gold, nitric acid, acetic acid, and ammonia.*"

The harmful effects of some of these chemical poisons are insidious and cumulative. More plainly evident is an allergenic skin response called dermatitis, resulting usually from the continued exposure of the skin to photographic solutions, particularly developers. An attack of dermatitis has been described by Miles J. Breuer, M.D.[34]:

> The eruption, after exposure to an irritating reducing agent, does not appear at once. Twenty-four to forty-eight hours elapse before any sign appears. Then, thick-walled vesicles (blisters) are seen, deep in the skin where it is thinnest, as between the fingers and on the wrists. In another day or two these come to the surface as red papules (solid pimples). In a day or two more, the skin between them becomes raised, thickened, and red. From the beginning there is constant itching, becoming more and more intense. The skin surface may become raw and discharge a thin, clear fluid. This is serum or lymph from the tissues underlying the skin, produced in excess because there is an increased amount of blood in the vessels, and coming to the surface because the outer layers of the skin have been destroyed. There is no essential difference in the eruptions produced by the various photographic reducing agents. The eruption runs a definite, self-limited course of ten days to two weeks; involution, regression, and complete recovery occur spontaneously.
>
> Once the eruption appears, there is no way of cutting it short, nor of preventing it from running its complete course. It goes through its full program to the bitter end, despite all efforts at treatment. Therefore the victim might as well make up his mind to suffer it through in patience instead of raising false hopes. In fact, ill-directed attempts at treatment may make it worse and prolong its course. The only treatment that can be recommended is some method of relieving the itching and burning. This will prevent the patient from scratching or rubbing the eruption, and hasten his recovery if such a thing is possible.

Obviously, the use of solutions containing nonallergenic developing agents would avoid dermatitis. Developers with *p*-aminophenol[35] or

Amidol[36] have been suggested as replacements for Metol. Phenidone is now widely used as a nontoxic replacement for Metol. But once contracted, photographic dermatitis needs relief, if not a cure. Everything from X-rays[37] to soaking the hands in hot water[38] has been proposed, but most of the treatments involve ointments. Dozens of formulations have been suggested in the photographic press.[39–52] One representative formulation[53] contained

Ichthyol	1 part
Resorcin	1 part
Glycerine	1 part
Zinc oxide	1 part
Paraffin ointment	6 parts

The *British Journal Photographic Almanac*[54] suggested

Ichthyol	1 part
Lanoline	4 parts
Boric acid	4 parts
Vaseline	3 parts

Inflammation of the skin, or dermatitis, may be an allergenic reaction that is acquired after repeated contact with a specific chemical. Some people are much more resistant than others; some may lose their resistance with time as the skin undergoes changes due to repeated contact with the chemical. Once sensitized, an individual's skin may swell or redden upon even slight contact with the chemical. This type of skin allergy, often referred to as Metol poisoning, has been widely discussed.[55–58] The actual poisonous agent has been said by W. F. A. Ermen[59–60] to be an impurity—*N*,*N*′-dimethyl-*p*-phenylenediamine—in the Metol. Free *p*-phenylenediamine has been shown to cause dermatitis whether it is present in dyed furs[61] or in photographic developers.[62–64] Other developing agents, such as Amidol or hydroquinone, or their oxidized forms, have been reported to be toxic. In alkaline solution, developing agents such as Amidol, Metol, and the *p*-phenylenediamines are present as free bases—fat-soluble substances that can permeate through the skin even though the tough keratin outer layer is unbroken.

Actually, one of the causitive agents in a photographic developer is the alkali. Alkali causes the skin to be dry, to peel or crack. These breaks in the skin allow easy penetration of the poisonous chemicals. Prevention of dermatitis should start with the neutralization of any alkaline solution that contacts the skin.[65–71] Soaking the hands in a mild acid solution, such as a 3% solution of acetic acid or a stop bath, after each contact with an alkaline solution will greatly minimize the danger of skin cracking. Body fluids are alkaline, so that mild acids are quickly neutralized. Alkaline fluids in contact with skin are dissipated by slow absorption into the tissues. Damage may be

done during this slow process, so that neutralization of the alkali by an external acid solution is required if the skin is to be maintained in a healthy condition. Obviously, if possible, the alkaline solution should be kept from contact with the skin. Rubber gloves are recommended for this purpose. Barrier creams have been reported to be ineffective against contact with color developing chemicals.[72] Especial care should be taken not to splash strongly alkaline color developers on the sensitive tissues of the face. The eyes should be protected by glasses or a shield. Breathing of poisonous vapors such as acids, ammonia, carbon tetrachloride, chloroform, cyanides, formaldehyde, iodine, or sulfur dioxide should be avoided by adequate ventilation or the use of an exhaust hood.

Some chemicals that by themselves are relatively innocuous may react dangerously when combined with other chemicals.[73] It is impossible to list every possible hazardous combination, but the following should be avoided.

Do not combine	*with*
Acetic acid	Chromic acid, nitric acid, perchloric acid, peroxides, and permanganates
Ammonia	Calcium hypochlorite or halogens
Ammonium nitrate	Acids, chlorates, nitrates, combustible materials
Chlorates	Acids, ammonium salts, combustible substances
Chromic acid	Acetic acid, alcohol, glycerine, flammable liquids
Cyanides	All acids
Hydrogen peroxide	Most metals (especially chromium, copper, and iron) and their salts, flammable fluids, and combustible materials
Iodine	Ammonia
Nitric acid	Acetic, chromic, or hydrocyanic acids; flammable substances
Oxalic acid	Silver
Perchloric acid	Acetic anhydride, alcohol, bismuth, organic materials
Potassium permanganate	Glycerine, ethylene glycol, benzaldehyde, and sulfuric acid
Sodium peroxide	Glacial acetic acid, acetic anhydride, alcohol, benzaldehyde, glycerine, ethylene glycol, ethyl acetate, or any oxidizable substance
Sulfuric acid	Chlorates, perchlorates, and permanganates

Probably the best advice concerning the handling of photographic chemicals is that of E. Wagner[74]: "Since absolutely non-poisonous substances do not exist, no precaution should be omitted during work with chemicals."

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Chapter 8
Fine-Grain Developers

By far the greatest factor in the graininess problem is the character of the film emulsion itself.

LLOYD E. VARDEN[118]

Modern development of black-and-white negative films is concerned with ever smaller negatives, especially the 35mm and $2\frac{1}{4} \times 2\frac{1}{4}$-in. sizes. The increasing use of these small-format films has had a profound effect on film-making technology. The emulsion maker has striven to produce small silver bromoiodide crystals of the highest-possible light sensitivity. Crystal size distribution has been closely controlled. The coagulation of the crystals has been minimized during both the making and coating operations. Two-layer coatings, consisting of two emulsion compositions of different light sensitivity, so common during the early years of the miniature camera, have often been replaced by thin, single-layer coatings of exceptional compactness. Even two-layer film coatings are exceedingly thin. These refinements of emulsion making and coating have enabled today's films to provide minimum graininess while maintaining high sensitivity to light.

Fine-grained photographic images start with the emulsion maker. J. S. Friedman[1] has stated the emulsion maker's problem. He calculated that in a high-speed negative emulsion the average length and width of a silver halide grain was about 0.95 μ (10,000 μ in 1 cm). This same emulsion contains 22.61×10^9 grains/cm^3. In a straight line this is somewhat less than 3000

grains/cm. The distance between any two grains was then estimated by Friedman to be 3μ, the clear space between the grains being three times the space occupied by the grains. Although this clear space would tend to be filled by grains at different levels throughout the depth of the coated emulsion layer, sufficient clear space is still present so that much light (estimated at about 25%) will pass through without effective use—not only light unimpeded by the layer but also light reflected and scattered by the silver halide crystals in the layer.

Practical photographic emulsions consist of a range of silver halide particles of various sizes. Larger grains are inherently no more sensitive than smaller grains. The larger the grain size, however, the greater the light-collecting area, and the greater the probability that the entire crystal would become developable after exposure. The larger grains provide the greatest amplification, because the larger crystal size has the greatest number of silver ions available for reduction. All grains cannot be of the same sensitivity, because all would develop at the same time, limiting the scale of tone gradation. (See Figure 1.)

For suitable rendition of a variety of tones by a photographic emulsion, the coated layer must contain a distribution of light sensitivities. In areas of high exposure the large, medium, and small grains have all received sufficient light exposure to develop. At intermediate exposure, the large and medium-size grains would be developable. At low exposures, corresponding to the shadow areas of the negative image, only the large grains with their greater light-collecting surface could gather sufficient photo-generated electrons to form stable latent images. The photographic image formed by development is a discontinuous dispersion of granular particles, the larger masses of particles being formed from the larger grains. The smaller silver halide crystals with their smaller surface to collect light require greater exposure to form developable latent images but produce a finer metallic silver image. Thus, although emulsion granularity may be related to its sensitivity, this is a great oversimplification of a complex relationship.

Fine-grain developers are designed to produce the minimum granularity dependent upon the emulsion maker's distribution of the silver halide grain sizes. Speed-graininess characteristics are largely predetermined by the emulsion maker, so that efficient fine-grain developers seek to maintain the emulsion characteristics rather than radically change them. Emulsion speed is usually decreased by fine-grain development, and image sharpness may be decreased. The extent of these degradations is a measure of the effectiveness of a fine-grain developer. All claims for improved fine-grain developing formulations should be evaluated in terms of emulsion speed, graininess, and image sharpness, as true advances in photographic chemistry and emulsion chemistry are slow to evolve.[2]

Developing solutions for producing fine-grained images should reduce the silver from each grain in place in the gelatin layer. To achieve this aim, the solution must be relatively low in alkalinity. Highly alkaline solutions cause the gelatin of the emulsion layer to swell and soften more than solutions at lower pH. High alkalinity also causes a more rapid and vigorous formation of silver filaments. Both the softened gelatin and the vigorous formation of the silver particles increase the possibility that the silver filaments will be larger and more nonuniform in distribution.

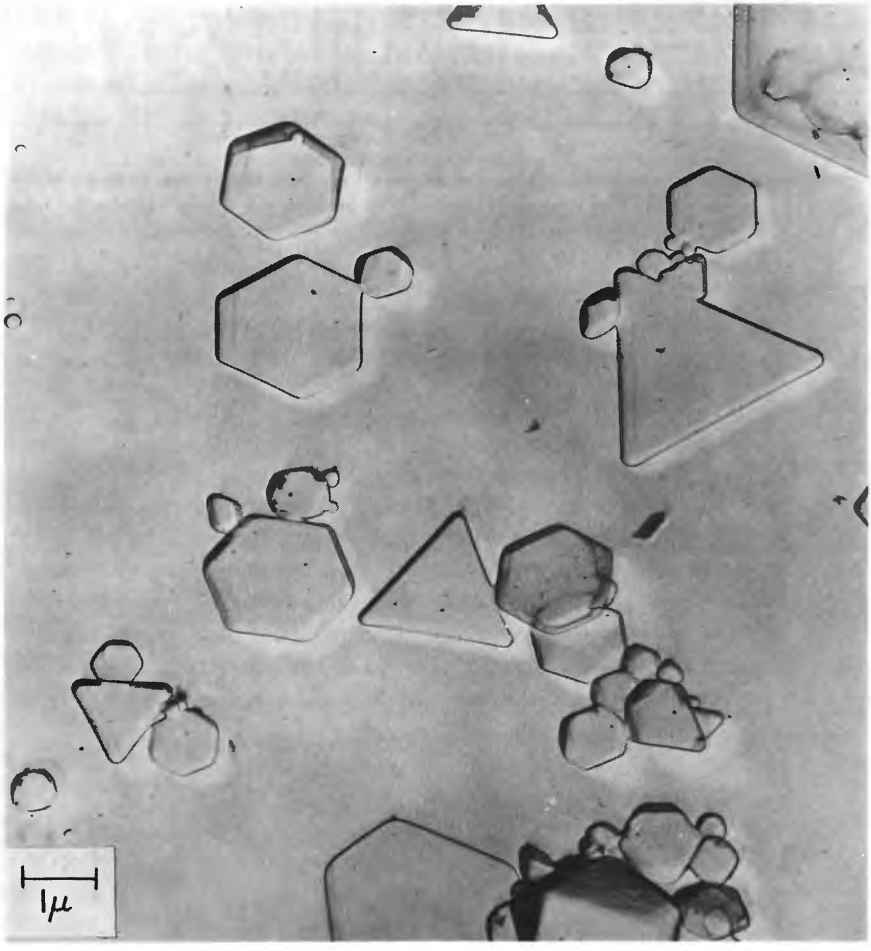
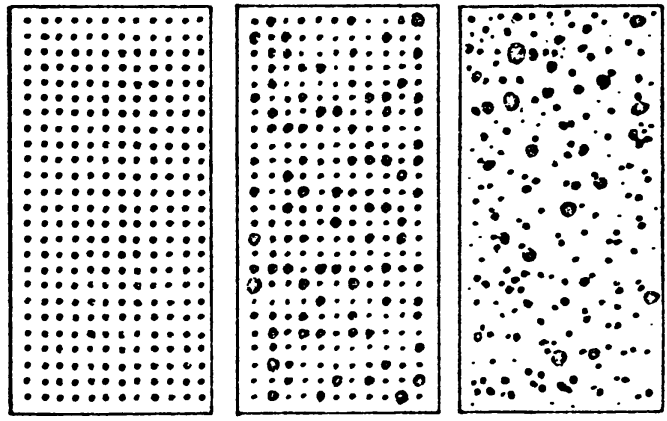


Figure 1. This electron micrograph of the undeveloped grains of a photographic emulsion shows the considerable variation of size often found in practice, thus adding inhomogeneity to the emulsion layer. [J. F. Hamilton, *App. Opt.*, 11: 18 (1972)]



(a) *(b)* *(c)*

Figure 2. Graininess involves both the size of the grains and their distribution, as shown in this schematic representation. A regular distribution (*a*) of uniform size grains exhibits the least inhomogeneity. Varying the grain size (*b*) decreases the homogeneity, as does irregular distribution of grains of various sizes (*c*). This latter condition is found in photographic emulsions. [Lloyd E. Varden, *J. PSA*, 6 (3): 9 (1940).]

It is the lack of uniform distribution of the silver filaments that the eye sees as graininess, that mottled appearance that is most evident in the intermediate densities of the silver image.[3] Thick emulsion layers increase the possibility of graininess because they provide greater depth for the overlapping of the silver particles. In a region of minimal exposure the developed image will be located near the surface, and there will be less probability of optical clumping. With full exposure or overexposure the image will extend deeper into the emulsion layer, increasing the probability of image nonuniformity by overlapping silver particles in depth. Thus, the degree of exposure influences the graininess of the developed image. Minimum exposure of thin layers of fine silver halide grains is favorable for minimizing graininess. (See Figure 2.)

Developing a film emulsion to a high contrast means forming large deposits of silver in many areas of the film, thus emphasizing the nonuniform distribution of silver filaments. Maximum contrast is achieved when the entire grain is reduced to metallic silver, giving a high amplification of the latent image. Graininess is increased. Fine-grain development often effects a compromise by using photographic emulsions of fairly large silver halide crystals to secure good light sensitivity, then developing to a low contrast in order to limit the size of the deposits of silver filaments. By developing less than is possible, some sacrifice is made of the potential emulsion speed

obtainable from the silver halide crystals but the extent of the silver deposit is limited. (See Figure 3.)

Fine-grain developers are usually of two types: (1) low-alkalinity solutions that yield normal emulsion sensitivity with low-contrast images, or (2) low-alkalinity solutions that contain a silver halide solvent to dissolve some of the surface of the silver halide grains, resulting in a loss of emulsion sensitivity. Some of the dissolved silver from both the exposed and unexposed grains is deposited by solution-physical development on the filaments of metallic silver produced by direct chemical reduction at the latent image sites. Generally, the first type of fine-grain developer is a Metol-hydroquinone (MQ) or Phenidone-hydroquinone (PQ) solution that may also contain sodium sulfite as a silver halide solvent. Only part of the exposed silver halide crystals are directly reduced to silver filaments, and developing action is curtailed. The second type of developer often contains only Metol with

Figure 3. Texture and fine detail, as in this photograph of a Persian cat, can be effectively recorded through the use of a fine-grain developer giving detail-enhancing edge effects. (Photograph by Grant Haist)

considerable amounts of sulfite or other silver halide solvent, or it may be based on the silver-solvent developing action of *p*-phenylenediamine. Some of the silver halide crystal is dissolved before chemical reduction is completed. *p*-Phenylenediamine is often used in combination with other developing agents, especially Glycin, to help overcome some of the loss of emulsion sensitivity given by the solvent developing agent that forms image silver of fine particle size but low light-stopping power.

METOL-HYDROQUINONE FINE-GRAIN DEVELOPERS

The Elon-hydroquinone-borax developer known as Kodak developer D-76 was devised by J. G. Capstaff[4,5] in 1926. This formulation produced maximum shadow detail with a low-contrast image. Today, this solution is often the standard against which other formulations are rated. The formulation of this developer has been widely adopted by others: Ilford ID-11 is identical, and Gevaert G-206 contains one less gram of hydroquinone. Adox MQ and Ansco 17 represent variations of the basic formulation. Developer D-76b is a softer-working version of D-76.

H. C. Carlton and J. I. Crabtree[6] have found that "The results for any time of development show that with the regular borax developer (D-76) the rate of development increased with keeping. The gamma for 12 minutes development increased from 0.78 to 1.19 in 49 days. With the buffered developer (D-76d) the rate of development remained constant within the limit of error for the 49 days of keeping. For sensitometric purposes which depend upon the development factors remaining constant over a period of several weeks, the buffered borax developer is preferable to the regular formula." (See Table 2 for the formula of Developer D-76 and others.)

D-76 developer has been proposed for one-time use only, then to be discarded. This procedure avoids the possible change in activity of the used developer upon standing. Such a technique may be uneconomical for some if the developer is purchased in less than one-gallon quantities, but the mix-your-own cost involves only a few cents for each roll of film. Dilution of one part of the full strength D-76 developing solution with one part of water provides an economical one-use working solution. Dilution of D-76 with an equal volume of water is now a widespread modern photographic practice, requiring about a 40% increase in the developing time over that required for the undiluted developer. The diluted developer has a contrast-flattening or compensating effect that is particularly useful for processing negatives taken under contrasty lighting conditions.[7,8] Richard W. Vesey[9] has suggested that the original processing time for the undiluted developer can be maintained if the 1:1 solution of the developer is six degrees warmer than the temperature for the undiluted developer. A table of processing times for

Table 1. D-76 Processing Times[a] with Popular 35mm Films

Film	Index	Time
Adox KB-14	32	7 min (1:1 dil.)
KB-17	64	8 min (1:1 dil.)
KB-21	200	9 min (1:1 dil.)
Agfa Isopan FF	32	7 min (1:1 dil.)
F	40	7 min (1:1 dil.)
SS	125	10 min (1:1 dil.)
Ultra	400 to 650	10 min (straight)
Record	1600	13 min (straight)
GAF Versapan	125	5½ min (straight)
Hypan	500	12 min (1:1 dil.)
Hypan	500	7 min (straight)
Ilford Pan F	32	7 min (1:1 dil.)
FP3	125	9 min (1:1 dil.)
HP3	400	12 min (1:1 dil.)
HPS	800	12 min (straight)
Kodak Panatomic-X	50	7 min (1:1 dil.)
Panatomic-X	50	4½ min (straight)
Kodak Plus-X Pan	125	7 min (1:1 dil.)
Plus-X Pan	125	4½ min (straight)
Kodak Tri-X Pan	650	11 min (1:1 dil.)

[a] Processing times given here are for 68°F with continuous agitation for the first 30 sec and 5 sec each minute thereafter.

various types of 35mm film, compiled by Vesey, is reproduced here (Table 1), as it shows processing times for the 1:1 dilution of D-76.

Michael Edelson,[10] as well as Vesey, has observed that undiluted D-76 is equally effective over a range of processing temperatures. Edelson has written that

If, for example, the basic time is nine minutes at 68°F, the range would be as follows:

69°F	8¾ minutes	78°F	5¼ minutes
70°F	8¼ minutes	80°F	4¾ minutes
72°F	7½ minutes	82°F	4 minutes
75°F	6½ minutes	85°F	3 minutes

These figures . . . are to be used with agitation for the first 30 seconds of development and for five seconds every 30 seconds thereafter.

Control of the degree of agitation is essential, as the D-76 developing solution has been reported to be particularly affected by it. For example, Vesey noted that

> The contrast of any film can be increased or decreased the equivalent of one grade of printing paper by altering the agitation rate as follows:
>
> *To Increase Contrast:* Agitate the film continuously for the first minute and then at 30-second intervals for the remainder of the processing time.
>
> *To Decrease Contrast:* Agitate the film continuously for the first 15 seconds of processing and then for two or three seconds every minute of the remaining time.

Normal agitation was continuous for the first 30 sec and for five seconds of each minute of the remaining time.

The Elon-hydroquinone-borax composition of D-76 increases in alkalinity with aeration with keeping or after some use. This results in increased development, so that results are often inconsistent. Even the normal aeration of mixing will make it difficult to achieve exactly the same results from two solutions of this developer, an unfortunate property for a standard developer. This lack of buffering may be overcome by adding four times the normal borax and 8 g of boric acid to the D-76 formulation. This developer, D-76d, gives essentially the same graininess as D-76 at the same developing times.

The introduction of D-76 developer (known as the Eastman borax developer at that time) caused photographic investigators everywhere to study the nature of its fine-grain properties. A summary of some of this early work was given by H. C. Carlton and J. I. Crabtree:[6]

> Its ability to produce fine-grained images is undoubtedly a result of the presence of a high content of sodium sulfite which exerts a solvent action on the silver halide grains reducing their size and preventing clumping.[11] Namias[12] concludes that the rate of development is too low for practical purposes and claims that his recommended developer . . . [five grams of Metol, fifty grams of sodium sulfite, and five grams of sodium carbonate in a liter of water with 5 ml of phenosafranine (1:1000) present] . . . gives equally fine-grained images with an increase in the rate of development. Lumière and Seyewetz[13] found that the images produced by borax developer are finer grained than those produced by the same developing constituents used with carbonate as the alkali. Veldman[14] concluded that the borax developer gave very fine-grained images but no finer than the following developer: Elon 15 grams; sodium sulfite (anhydrous) 150 grams; potassium bromide 2 grams, water to 1 liter. This developer is impractical because of the loss in emulsion speed caused by the high bromide content. He varied the sulfite content from 0.5 to 320 grams per liter and found that the graininess decreased as the sulfite content increased. Luppo-Cramer[15] found with the Eastman borax developer that fine-grained images were not obtained with all silver bromide emulsions. Emmermann[16] in a series of tests on motion picture film found that the Eastman borax developer was the best formula known for producing fine-grained images. Nauck[17] concludes that the low alkalinity of the borax developer contributes indirectly to the

production of fine-grained images because the relatively low rate of development permits the sulfite to exert more solvent action which progresses with time."

Other studies of the Metol-hydroquinone-borax developer have been made.[18,19]

Modern research techniques have been used to study the nature of the development given by the D-76 developer. The combination of low alkalinity and high sulfite concentration is responsible for the fine-grain characteristics of the solution. Reducing the sulfite also led to a loss in speed.[7] G. I. P. Levenson[8] has found that "Optimum emulsion speeds are obtained with a zero concentration of bromide." Thus, used D-76 may produce less film speed than the unused solution. Even modern research techniques have been unable to explain completely the unique properties of what is essentially a solution of Metol-free base in 10% sodium sulfite, the borax having been used to just neutralize the acidity of the Metol salt, and the hydroquinone being an ineffective developing agent at the pH of the solution.

Dissolve the chemicals in the order listed in Table 2. Filter the water to remove all foreign particles. Use distilled water, if possible. All water should be neutral (pH 7). If not, boil, then cool before mixing developer solutions.

Table 2. Developer Formulas

Ingredient[a]	Kodak D-76	Kodak D-76R[b]	Kodak D-76b	Kodak D-76d	Adox MQ	Ansco 17
Water (125°F or 52°C)	750 ml	750 ml	750 ml	750 ml	750 ml	750 ml
Metol	2	3	2.75	2	2	1.5
Sodium sulfite (anhydrous)	100	100	100	100	80	80
Hydroquinone	5	7.5	2.75	5	4	3
Borax	2	20	2.5	8	4	3
Boric acid	—	—	—	8	—	—
Potassium bromide	—	—	—	—	0.5	0.5
Water to make	1 liter	1 liter	1 liter	1 liter	1 liter	1 liter
Dev. times (min) (68°C or 20°C)	9 to 17				10 to 19	10 to 20

[a] All ingredient quantities are in grams unless indicated otherwise.

[b] Add 30 ml of D-76R solution for each 120 or 36-exposure, 35mm roll of film processed in the D-76 developer, discarding the used D-76 solution, if necessary, to maintain the original solution volume.

PHENIDONE FINE-GRAIN DEVELOPERS

Phenidone in combination with hydroquinone may be used to produce fine-grain developers of good keeping properties. Such developers exhaust well because the small quantity of Phenidone present is not used up but is regenerated by the greater amounts of the hydroquinone present. Ilford Developer ID-68 is a buffered borax PQ solution that has good stability with use, producing a small film speed increase over D-76 with only a slight increase in graininess.

Ilford Fine Grain Developer ID-68

	ID-68	ID-68R
Warm water (125°F or 50°C)	750 ml	750 ml
Sodium sulfite (anhydrous of desiccated)	85 g	85 g
Hydroquinone	5 g	8 g
Borax	7 g	7 g
Boric acid	2 g	—
Phenidone	0.13 g	0.22 g
Potassium bromide	1 g	—
Cold water to make	1 liter	1 liter
Dilution	0	Add to ID-68 to maintain level
Time	8 to 10 min, 68°F	

The photographic properties of Phenidone were first investigated by J. D. Kendall,[20] who has proposed a fine-grain Phenidone developer for films and plates.[21] The developer had characteristics similar to those of Ilford ID-11 (same as D-76) but showed less variation in activity during use. The chemical constituents are to be dissolved in hot water (around 120°F) in the order given.

Sodium sulfite, anhydrous	100 g
Hydroquinone	5 g
Borax	2 g
Boric acid	1 g
Potassium bromide	1 g
Phenidone	0.2 g
Water to make	1 liter
Development time	7 to 11 min, 68°F

The accumulation of bromide in a low-pH MQ developer solution can adversely affect the developer's activity. Phenidone-hydroquinone developers of low pH, however, are little affected by the accumulation of bromide during use of the solution. A. J. Axford and J. D. Kendall[22] note that "the PQ developer may be used long after the bromide concentration has risen to a value which would make a corresponding MQ developer useless."

Geoffrey W. Crawley[23] devised a series of modern developer formulas, the "FX" series, in which FX-3 was a PQ equivalent of D-76 with an approximate 30% film-speed gain and FX-4 a composition yielding a near 60% gain. Developer FX-3 was reported to show an increase in developing activity after standing or reuse similar to that encountered with D-76. FX-18 provides normal or slight speed increases with a more compact grain pattern than MQ borax formulas.[24] It can be employed at 1:1 dilution as a one-use solution.

	FX-3	FX-4	FX-18
Water (125°F or 50°C)	750 ml	750 ml	750 ml
Metol	—	1.5 g	—
Sodium sulfite, desiccated	75 g	100 g	100 g
Hydroquinone	6 g	5 g	6 g
Phenidone	0.25 g	0.5 g	0.10 g
Borax	2.5 g	2.5 g	2.5 g
Sodium bisulfite	—	—	0.35 g
Potassium bromide	1.0 g	0.5 g	1.6 g
Water to make	1 liter	1 liter	1 liter
Dilution	0	0	0 or 1:1
Times (68°F or 20°C)	4 to 11 min	4 to 10 min	8 to 20 min (1:1) 6 to 14 min

METOL-SULFITE FINE-GRAIN DEVELOPERS

In MQ developers of low alkalinity most of the reduction of silver is accomplished by the Metol, as the hydroquinone is only weakly ionized and almost inactive under these conditions.[25,26] The small contribution of the hydroquinone may be made up by simply increasing the Metol concentration.[27] Aeration of Metol-hydroquinone-borax developer of low alkalinity, pH 8.4 to 8.8, causes an increase in activity, but low-alkalinity Metol developers show almost no change in activity.[28] Metol is active in the weak alkalinity of a sodium sulfite solution. In 1944 R. W. Henn and J. I. Crabtree[29]

Table 3. Developer D-23[a]

Formulary

Spoon formula

Water	$\frac{3}{4}$ quart (24 oz.)
Metol	2 tsp
Sodium sulfite, desiccated	4 Tbs + 1 tsp
Water to	1 quart (32 oz.)

Metric formula

Water	750 ml
Metol	7.5 g
Sodium sulfite, desiccated	100 g
Water to	1 liter

Development Times[b]

Film	Meter Setting	No Dilution	Diluted 1:3
Ilford Pan F	50	6	14
Ilford FP4	125	$6\frac{1}{2}$	$14\frac{1}{2}$
Ilford HP4	400	$6\frac{1}{2}$	$14\frac{1}{2}$
Kodak Panatomic-X	32	6	14
Kodak Plus-X	125	6	14
Kodak Tri-X	400	$6\frac{1}{2}$	$14\frac{1}{2}$
Kodak H.S. Infrared	—[c]	$6\frac{1}{2}$	$14\frac{1}{2}$

Push-Processing Development Times

Ilford HP4	800	$12\frac{1}{2}$
Ilford HP4	1600	20
Kodak Tri-X	800	$12\frac{1}{2}$
Kodak Tri-X	1600	20

[a] Diluted D-23 consists of one part developer solution mixed with three parts water.

[b] All development times are given in minutes at 68°F with constant agitation.

[c] Meter settings as recommended in instructions.

Source: Mike Brenner, *Petersen's PhotoGraphic Magazine*, April, 1975. Courtesy Petersen Publishing Company, Los Angeles, Calif.

introduced the formula for Kodak Developer D-23, although Metol-sulfite developers were proposed before that time. For example, in 1934 Rudolph von Erhardt proposed a fine-grain developing solution containing 15 g Metol and 100 g anhydrous sodium sulfite in a liter of water. In 1938 Hans Windisch published a compensating developer formula consisting of 1000 ml of boiled water, 2.5 g of Metol, and 50 g of sodium sulfite crystals.[30] The simplicity of the D-23 developer—7.5 g of Metol and 100 g of anhydrous sodium sulfite per liter of water solution—produced a moderately low contrast at the times of development of D-76 with a loss of 10–20% of the film emulsion speed normally given by the D-76. This slight loss of shadow detail was said to be relatively unimportant. Image graininess was slightly less than with D-76. (See Table 3.)

The same researchers found that lowering the alkalinity of a Metol-sulfite developer decreased the activity, as expected, but the graininess was markedly decreased. The very fine-grain characteristics of this developer were ascribed to the solvent action of the sodium sulfite. Sodium bisulfite was selected to lower the pH of the D-23 Metol-sulfite developer because the sulfite-bisulfite formed an efficient buffer mixture for the alkalinity range of the developer. The addition of 15 g of sodium bisulfite to the D-23 formulation produced the most desirable results. Processing at 77°F (25°C) made the time of development about the same as for D-76 or D-23 at 68°F. Film emulsion speed was only about 50 to 60% of that given by D-76 development. However, graininess was considerably less and was said to be comparable to that given by *p*-phenylenediamine developers but without their toxicity. The pH of the Metol–sodium sulfite–sodium bisulfite developer, called Kodak Developer D-25, is 7.0, providing a minimum of gelatin swelling even at the 77°F processing temperature.

The introduction of developers D-23 and D-25 has been followed by many variations using Metol with a high concentration of sodium sulfite. (See Table 4.) Some of these modifications also used small quantities of an alkaline substance to increase the alkalinity of the solution above the pH given by the sulfite, such as sodium carbonate in Agfa 14 or buffered borax in FX-5. MCW Rapid Developer containing 5.5 g Metol, 75 g anhydrous sodium sulfite, and 5 g sodium perborate (sodium metaborate) in 600 ml water has been claimed to give a 50% speed increase over D-76 development with slightly less and more even graininess.[31,32] Development times at 77°F in MCW Rapid were about half those of D-76 used at 68°F.

These developers utilize high concentrations of sodium sulfite as a solvent to etch away the surfaces of silver halide grains, producing fine silver particles upon development and minimizing the clumping of these particles. Other solvents may be used. Ammonium chloride,[33–36] sodium chloride, potassium thiocyanate, sodium thiosulfate, and thiourea have been employed to achieve

Table 4. Solvent Fine-Grain Developers

Developer Ingredient[a]	Developer Formulas						
	Kodak D-23	Kodak D-25	M.C.W. Rapid	Agfa 14	Crawley FX-5	Kodak DK-20	Windisch W-22
Water (125°F or 50°C)	750 ml	750 ml	500 ml	750 ml	750 ml	750 ml	750 ml
Metol	7.5	7.5	5.5	4.5	5.0	5.0	8
Sodium sulfite, desiccated	100	100	75	85	125	100	65
Sodium bisulfite	—	15	—	—	—	—	—
Potassium metabisulfite, crystal	—	—	—	—	—	—	7
Kodalk	—	—	5	—	—	2	—
Sodium carbonate, anhydrous	—	—	—	1	—	—	—
Potassium bromide	—	—	—	0.5	0.5	0.5	—
Potassium thiocyanate	—	—	—	—	—	1.0	—
Borax	—	—	—	—	3	—	—
Boric acid	—	—	—	—	1.5	—	—
Water to make	1 liter	1 liter	600 ml	1 liter	1 liter	1 liter	—
Development time (min) (68°F or 20°C)	10 to 12	20 11 (77°F)	5 (77°F)	—	8 to 12	—	8 to 15

[a] Quantities of developer ingredients are given in grams unless indicated otherwise.

fine-grain development. The silver-solvent action and development restraint of potassium bromide yields fine grain but with severe losses in emulsion speed of the photographic material. (See Figure 4.)

The presence of a thiocyanate in an MQ developer produced low graininess, according to the 1937 experiments of Strauss, but fog was increased.[37] In 1938 the Kodak Fine Grain Developer DK-20 was formulated by J. I. Crabtree and R. W. Henn,[38] using potassium thiocyanate-sodium sulfite with Metol as the sole developing agent. Sodium metaborate (Kodalk) provided the alkali and potassium bromide helped to minimize the fog. According to E. W. Lowe,[39] potassium thiocyanate in small amounts forms an insoluble silver salt and acts as a restrainer of development. At larger concentrations the potassium thiocyanate forms soluble silver complexes that result in excessive fog, possibly by physical development. For producing

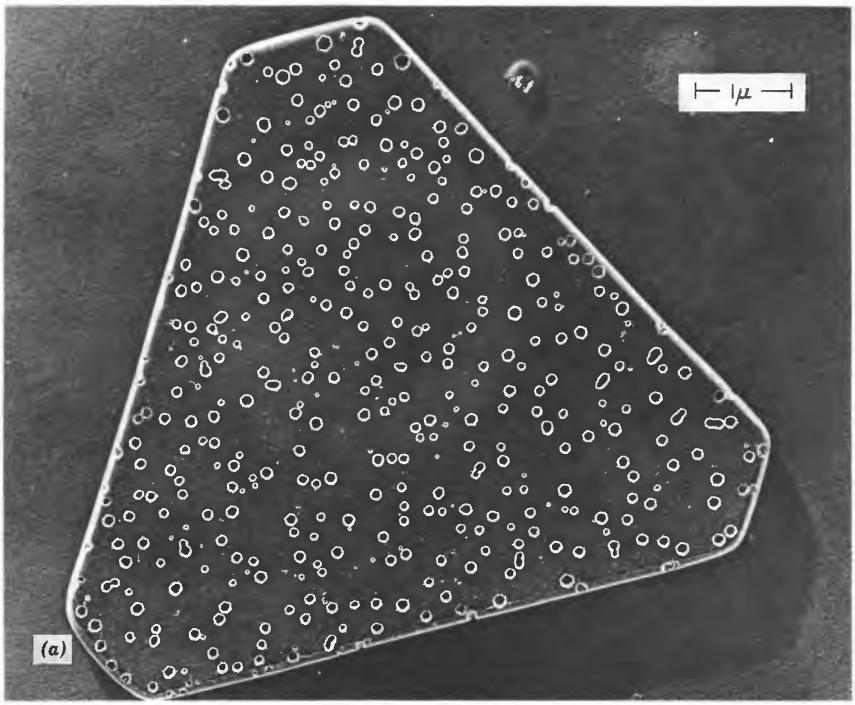


Figure 4. The nature of the etching of these large silver bromide grains is dependent upon the type of solvent used. The etch pits formed by potassium cyanide (*a*) differ from those of potassium bromide (*b*). The bromide was used to treat a grain under compressive strain, which was found to increase the number of pits as compared with an unstrained grain. [J. F. Hamilton, L. E. Brady, and F. A. Hamm, *J. App. Phys.*, 29: 801–802 (1958)]

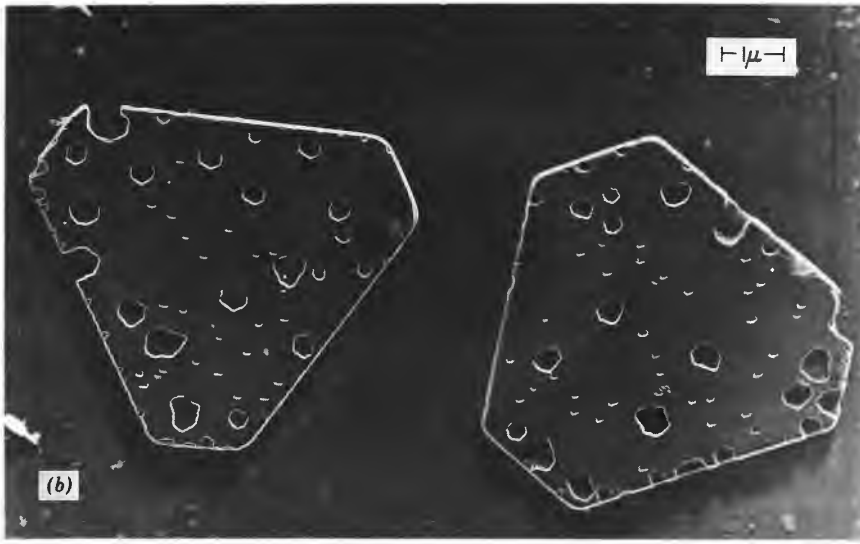


Figure 4. (*continued*)

fine grain, the best concentration is the largest amount of thiocyanate that can be added without causing the undesirable fog. The desired quantity of thiocyanate depends upon the alkalinity and composition of the developing solution. The DK-20 developer produces graininess considerably less than D-76 with about a 35 to 50% loss of film emulsion speed. This solvent approach to fine-grain development is currently little used, as thiocyanates may produce scumming on the surface of present-day film materials. In addition, the silver halide grain size of modern fine-grain film emulsions does does not require the size reduction needed by the larger-grain emulsions of previous years. Solvent developers might be most useful with the higher-speed, medium-to-large silver halide crystals in today's higher-speed materials if the speed loss could be tolerated.

OTHER SOLVENT FINE-GRAIN DEVELOPERS

The use of a silver halide solvent in a developing solution has been one of the major methods to obtain fine-grain silver images. Sodium thiosulfate, which was studied before the turn of the century for its effect in developing solutions, is a logical choice for a solvent in fine-grain developers. In 1929 H. C. Carlton and J. I. Crabtree[6] found that the addition of a small concentration of thiosulfate to a borax developer decreased the rate of development and the

speed of the emulsion. They concluded, "Hypo is a very active silver halide solvent and the concentration that can be used is critical. One gram per liter was sufficient to produce very fine-grained images. The higher concentrations, although giving satisfactory graininess, dissolved so much of the silver halide that they appreciably decreased the speed of the emulsion." They added, "The advisability of the use of hypo in this type of developer, however, is questionable."

P. K. Turner,[40] seeking an alternative to the slow-acting but fine-grain physical developers, added sodium thiosulfate to the D-76 developer formulation. The Turner Solvent Developer, as it was originally called, became the M.C.W. 1 Developer, the initials standing for *Miniature Camera World*, the magazine in which the formula appeared. M.C.W. 1 was made by adding three parts of sodium thiosulfate per 1000 parts of the regular D-76 solution. This was best done by adding 6 ml of a 50% solution of sodium thiosulfate per 1000 parts of the D-76 developer. Alternatively, the M.C.W. 1 Developer could be made from the following formula:

M.C.W. 1 Developer

Metol	2 g
Hydroquinone	5 g
Sodium sulfite, desiccated	100 g
Borax	2 g
Sodium thiosulfate pentahydrate	3 g
Water to make	1 liter

This modified D-76 was said to give slightly less emulsion speed than D-76 with about half the graininess. Less fog and a less warm-toned image were also yielded by the M.C.W. 1 developer, using essentially the same times of development as D-76.

The M.C.W. 1 formula was then modified to produce a one-time-use developer that was more economical.[41,42] This developer, called M.C.W. 2, produced essentially the same emulsion speed as D-76 with finer graininess than D-76 but not as fine as given by M.C.W. 1. One part of M.C.W. 2 was added to seven parts of water to make the working solution. A less concentrated version of this developer, called M.C.W. 2a, was also proposed.[43] This developer stock solution was diluted one part of the developer to five parts of water, making six parts in all. The development time for most films was practically the same as for D-76 developer. If the dilution of the developing solution is varied, the more thiosulfate gives less emulsion speed and finer

grain and vice versa. The formulas for M.C.W. 2 and M.C.W. 2a are as follows:

	M.C.W. 2	M.C.W. 2a
Metol	4 g	3 g
Hydroquinone	8 g	6 g
Sodium sulfite, desiccated	40 g	30 g
Sodium metaborate	16 g	12 g
Sodium thiosulfate pentahydrate	24 g	18 g
Water to make	1 liter	1 liter
Dilution for use (developer:water)	1:7	1:5

An all-purpose developer, called M.C.W. 3, was formulated by M. L. Haselgrove for use as a film or paper developer.[44] The basic formula consisted of four solutions:

Solution A—Developer Stock Solution

Metol	2 g
Hydroquinone	7 g
Sodium sulfite, desiccated	60 g
Sodium metaborate	6 g
Water (boiled) to make	1 liter

Solution B—10% Potassium Bromide

Potassium bromide	100 g
Water to make	1 liter

Solution C—10% Sodium Carbonate

Sodium carbonate, crystals	100 g
Water to make	1 liter

Solution D—10% Sodium Thiosulfate

Sodium thiosulfate pentahydrate	100 g
Water to make	1 liter

For film development, add one part of solution A and five parts of water to make working developer. The same development times as recommended for D-76 development will produce less emulsion speed but finer-grained images. Up to 30 ml of solution D may be added to each liter of the diluted developer stock solution to produce a solvent developer, giving even finer grain but with more loss of film speed. Such a thiosulfate-containing developer should not be used with films that are already very fine in grain, because the speed loss will become excessive. For the development of photographic paper the recommended formulation consists of

Solution A	100 ml
Solution B	2 ml
Solution C	80 ml
Water to make	200 ml

Develop for $1\frac{1}{2}$ to 2 min minimum at 68°F.

Ammonium chloride had been highly recommended in 1904 by A. and L. Lumière and A. Seyewetz[33,34] as a solvent for making fine-grain developers. In 1936, John I. Crabtree and Paul W. Vittum[45] patented the addition of about 50 g of ammonium chloride to a liter of an MQ developer to produce a fine-grain developing solution. A suitable formula consisted of

Metol	2 g
Hydroquinone	5 g
Sodium sulfite	100 g
Ammonium chloride	50 g
Borax	2 g
Water to make	1 liter

Negatives with dichroic fog may result when out-of date film is processed in developers containing ammonium chloride. Later, Paul W. Vittum[46] stated that the MQ developer containing ammonium chloride was unstable upon aeration because of the loss of ammonia from the solution. He proposed to replace the ammonium chloride with acid salts (such as the hydrochloride, nitrate, sulfate, or acetate) of primary, secondary, or tertiary organic amines to form "a fine-grain developer which is stable toward aeration." Suitable amines included

Ethylamine hydrochloride
Ethanolamine hydrochloride
Ethylenediamine hydrochloride
Diethylamine hydrochloride
Diethanolamine hydrochloride
Triethylamine hydrochloride
Triethanolamine hydrochloride

An example of an amine-containing fine-grain developing solution contained

Metol	2 g
Hydroquinone	5 g
Sodium sulfite (desiccated)	100 g
Ethanolamine hydrochloride	75 g
Sodium metaborate	2 g
Water to make	1 liter

Primary amines were better than secondary amines for producing fine-grain images, and secondary amines were better than the tertiary amines. The alkyl amines were usually to be preferred over the alkanol amines. Any of the amines in a developing solution were claimed to yield finer-grain images than the developing solution without the amines.

In a 1973 U.S. Patent, Isao Shimamura, Yoo Iijima, and Haruhiko Iwano[47] summarized the current knowledge concerning the addition of amines to developing solutions as follows:

> The desirable properties of processing procedures for silver halide, black-and-white photographic materials reside in increased speed, high rate of development and fine grained silver image. The well known development accelerators are amine compounds, such as alkylamines (U. S. Pat. No. 2,196,037), aralkylamines (U. S. Pat. Nos. 2,496,903; 2,515,147; 2,541,889), phenoxyalkylamines (U. S. Pat. No. 2,482,546), heterocyclic alkylamines (U. S. Pat. No. 2,605,183), morpholine and piperidine (U. S. Pat. No. 1,086,681). These amines, however, are poisonous, odoriferous and volatile, thus necessitating careful handling. Furthermore, the deterioration in the granularity of the developed silver is often observed.

The strong physical developing action of many amines is responsible for the increase in silver particle size and the increase in fog. Shimamura, Iijima, and Iwano proposed the addition of nonvolatile imidazole to hydroquinone-containing developers for fine-grained silver halide materials, such as silver halide crystals from 0.1 to 0.3 μ. Such photographic materials are of slow speed but extremely fine grain, such as microfilm, high-resolution plates, positive film, or graphic arts film. The addition of imidazole to developing solutions for silver halide grains greater than 0.3 μ may have a detrimental effect on the fog and structure of the silver image. A developing solution containing

Water	800 ml
N-Methyl-*p*-aminophenol sulfate	1.0 g
Sodium sulfite	75 g
Hydroquinone	9 g
Sodium carbonate monohydrate	29 g
Potassium bromide	6 g
Imidazole	1 g
Water to make	1 liter

in 3 min, at 20°C, produced an increase in relative sensitivity with little increase in fog with a silver chlorobromide microfilm having less than 1% silver iodide and with a crystal size of less than 0.2 μ.

A high-energy, fine-grain photographic developer of the PQ type was formulated by Francis G. Berry[48] by adding aminoacetic acid or glycine (CH_2NH_2COOH) to the developing solution. Finer-grained images were also produced when aminoacetic acid was added to existing MQ or PQ developers. Berry's preferred formula was as follows (pH 8.54):

Sodium sulfite, anhydrous	100 g
Hydroquinone	10 g
Aminoacetic acid	10 g
1-Phenyl-3-pyrazolidone	0.4 g
Sodium borate	3 g
Boric acid	3.5 g
Potassium bromide	1.0 g
Water to make	1.0 liter

"The developer," according to Berry, "when mixed according to the formula shown above, has a higher threshold energy development than D-19, a very high energy developer, and finer grain characteristics than D-76, the generally accepted standard among fine-grain developers." For maximum speed and optimum development, a recommended time of development of 15 min at 68°F was made for most panchromatic films.

Most fine-grain developing solutions are slow acting, as such low-energy solutions produce silver images of fine particles which are not clustered or agglomerated. A rapid-acting but fine-grain developer would be desirable. Such a developing solution was said to be achieved by Albert L. Bunting[49] by using a dicarboxylic acid wetting agent, dibasic sodium borate, and a beta

naphthol, phenol, or naphthol sulfonic acid in an MQ developer at a pH of approximately 7.5. A specific example of this restrained developing solution consisted of

Metol	Approx. 1.75 g
Sodium sulfite	Approx. 90.0
Dibasic sodium borate	Approx. 6.5 g
Potassium bromide	Approx. 0.5 g
Aerosol O. T.	Approx. 2.0 g
Hydroquinone	Approx. 2.0 g
β-Naphthol	Approx. 0.5 g
Water to make	1.0 liter

Aerosol O.T. is a dicarboxylic acid sold by American Cyanamid Company. Other wetting agents were said to be equally effective.

Silver bromide and silver bromoiodide crystals are dissolved by sodium chloride present in a solution during development of the silver halides.[50] Ordinarily, chloride ions would be poor solvents for silver bromide or bromoiodides, but the presence of finely divided silver particles serves as a site for solution physical development, making chloride ions very effective silver halide solvents. When 100 g/liter of sodium chloride was dissolved in a Metol-sodium sulfite developing solution of low activity, the solution produced developed silver that was compact rather than the filamentary silver normally given by low-activity Metol-sulfite developers. The formation of the compact silver particles under these conditions was investigated by G. F. van Veelen and W. Peelaers.[51] They used a developing solution of pH either 7.0 or 8.5 containing

Metol	2 g
Sodium sulfite, anhydrous	2 g
Sodium chloride	None or 100 g
Sodium diphosphate	10 g
Water to make	1 liter

with three kinds of photographic emulsions:

1. Ultrafine cubic grain, silver bromide (0.07-μ average edge length).
2. Fine-grain silver bromide with 1% iodide content (0.25-μ average diameter).
3. Medium-grain silver bromide with 5% iodide content (0.55-μ average diameter).

Van Veelen and Peelaers concluded that

Sodium chloride, added in a high concentration to a developing bath of low activity dissolves silver bromide or iodobromide, when the silver chlorobromide complexes are quickly removed. This can be attained by adding active colloidal silver nuclei to the emulsion whereupon these complexes will be reduced. In the absence of nuclei practically no solvation of the silver halide is observed.

In the case of exposed emulsions the latent image can act as active nucleus. In Metol developers of low pH this reduction can be more important than the chemical development and compact silver with brown image tone will be formed.

Solution physical development was thought to be the cause of the compact silver particles and the brownish tone of the developed silver. When the concentration of the sodium chloride was 50 g/liter of developing solution, the developer produced filamentary silver particles that had been thickened by the solution physical development.

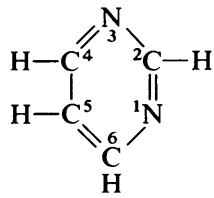
Fine-grain developing solutions containing common salt have been proposed. A formula suggested by Edgar Hyman[52,53] contained

Metol	5 g
Sodium sulfite, anhydrous	100 g
Common salt	30 g
Water to make	1 liter

Less salt was said to give more grain but higher film speed. A modification for one-time use has also been suggested.[54] The developing solution is diluted with an equal amount of water. "Tri-X rated at 400 ASA" was developed for 11 minutes at 68°F and said to give "Finer grain than D.76."

DEVELOPING SOLUTIONS CONTAINING PYRIMIDINE DEVELOPING AGENTS

Most developing agents require silver halide solvents or restrained activity to produce fine-grain silver images. *p*-Phenylenediamine is a developing agent that gives fine grain but is slow acting and toxic. Pyrimidines,



when substituted in the 2, 4, 5, or 6 positions with amino ($-NH_2$) groups or hydroxy (—OH) groups, have been claimed to act as fine-grain developing agents and to be less toxic than *p*-phenylenediamines.[55] An example of a pyrimidine fine-grain developing solution had the following composition:

Water	1 liter
4,5-Diamino-2,6-dihydroxypyrimidine sulfate	12 g
Potassium carbonate	80 g
Potassium bromide	0.2 g
Sodium sulfite	100 g

PHENYLENEDIAMINE DEVELOPERS

As early as 1904 A. and L. Lumière and A. Seyewetz[33,34] reported that of all the developing agents tested, only *p*-phenylenediamine and *o*-aminophenol, but not *p*-aminophenol, in sodium sulfite solution only produced truly fine grain without the need for additional silver halide solvents. A *p*-phenylenediamine developer dissolved 0.14 g of silver bromide and an *o*-aminophenol solution dissolved 0.134 g per 100 ml of developing solution. A sodium sulfite solution (6%) of a strength similar to that of the developing agents, but without these reducing agents, dissolved only 0.112 g of silver bromide. A *p*-phenylenediamine–sodium sulfite developer containing 10 and 60 g, respectively, per liter was suggested as the best developer to produce the finest-grained images.

The same authors[56] recommended the following fine-grain developer:

Sodium sulfite, anhydrous	60 g
p-Phenylenediamine	10 g
Trisodium phosphate	2 g
Potassium bromide	1 g
Water to make	1 liter

Development time was one hour, yielding a negative image of low density. Graininess, although fine, was greater than when *p*-phenylenediamine was used in weakly alkaline developing solutions.

Ammonium carbonate was used as an alkali for *p*-phenylenediamine developing solutions by Arthur Purdon.[57] Such a formula consisted of

Water	1 liter
Sodium sulfite, anhydrous	75 g
p-Phenylenediamine	10 g
Ammonium carbonate (10% solution)	5 ml

The presence of the ammonium carbonate was reported by Bland H. Casebolt[58] to increase the graininess of the *p*-phenylenediamine developing solution.

p-Phenylenediamine developers do produce very fine-grained images by physical development but with serious drawbacks: severe losses from normal emulsion speed, requiring four to six times normal exposure, long film immersion, and the toxicity and staining of the *p*-phenylenediamine and its oxidation products. To help reduce the huge losses of film emulsion speed, a second developing agent is often combined with the *p*-phenylenediamine. Glycin, which does not upset the fine-grain characteristics of the *p*-phenylenediamine, reduces the need to increase the film exposure more than two to three times the normal value. V. B. Sease[59,60] in 1933 formulated four developers with 90 g sodium sulfite and 10 g *p*-phenylenediamine in all four but with Glycin varying as follows: none in Sease No. 1, 1 g in Sease No. 2, 6 g in Sease No. 3, and 12 g in Sease No. 4 in one liter of water. The hydrochloride salt of *p*-phenylenediamine should not be used.

Most of the Sease developers are not suitable for modern films, but Sease No. 3, called Du Pont 21-D, may be suitable for some present-day emulsions. A *p*-phenylenediamine–Glycin version intermediate between Sease No. 2 and Sease No. 3, called Du Pont 5-D, contains 2 g of Glycin with 10 g of *p*-phenylenediamine base and 90 g of anhydrous sodium sulfite in a liter. This is an extremely fine-grain developer, especially with inherently fine-grained emulsions, but it still requires about twice the normal film exposure. Development times are from 30 to 40 min at 68°F (20°C).

Many *p*-phenylenediamine–Glycin fine-grain developing solutions have been proposed. P. W. Vittum and J. I. Crabtree[61] mentioned a formula consisting of 10 g of *p*-phenylenediamine and 12 g of Glycin in a liter of water containing 90 g of sodium sulfite (desiccated). A 1934 Edwal formula[62] consisted of

Distilled water (125 to 150°F)	500 ml
Sodium sulfite, anhydrous	37.5 g
p-Phenylenediamine	6 g
Glycin	6 g

Development time was 25 min at 70°F.

Most *p*-phenylenediamine-Glycin developers use the free base of *p*-phenylenediamine. William D. Fleming[63] used the hydrochloride salt but neutralized the hydrochloride by adding sufficient ammonium hydroxide. It was hoped that the resulting ammonium chloride would act as a solvent to minimize the increase in grain size normally found when alkali was added to the developing solution. This formula contained

Sodium sulfite, anhydrous	90 g
p-Phenylenediamine hydrochloride	16.8 g
Glycin	6.0 g
Ammonium hydroxide, normal (molar) solution	186 ml
Water to make	1 liter

Development time was 20 to 30 min at 68°F. In this and other formulas the *p*-phenylenediamine hydrochloride must be dissolved in hot water to solubilize the solid compound.

Metol may be added with *p*-phenylenediamine in developers, but this more energetic solution produces an increase in graininess. Even though *p*-phenylenediamine may initiate development in very low-pH solutions, it is thought that the second agent (Metol) will then carry out the reduction of the silver in the solution, whose alkalinity would not cause the Metol to start development. The developed silver thus loses its fine-grain characteristics given by the *p*-phenylenediamine and the grain becomes more characteristic of that given by the Metol. The Edwal 12 formula[64] (Metol–*p*-phenylenediamine–Glycin) is *p*-phenylenediamine activated, but the combined developing action at pH 7.5 does improve the emulsion speed over *p*-phenylenediamine developing solutions. (See Table 5 for the formula for Edwal 12.)

p-Phenylenediamine hydrochloride may be used, but an alkali must be added as in this formula proposed by E. W. Lowe.[65]

p-Phenylenediamine hydrochloride	12 g
Glycin	6 g
Metol	5 g
Sodium sulfite	90 g
Trisodium phosphate monohydrate	24 g
Water to make	1 liter

Table 5. Formulations of Some Fine-Grain Developers

Ingredient	Du Pont 5-D	Edwal 12	Windisch 665	MCM 100
Water	750 ml	1 liter	1 liter	1 liter
Metol	—	−6 g	12 g	—
Sodium sulfite (anhydrous)	90 g	90 g	90 g	90 g
p-Phenylenediamine (pure free base)	10 g	10 g	—	—
Glycin	2 g	5 g	—	—
o-Phenylenediamine	—	—	12 g	—
Meritol	—	—	—	16 g
Potassium metabisulfite (crystals)	—	—	10 g	—
Borax	—	—	—	2.3 g
Trisodium phosphate	—	—	—	6.9 g
Potassium bromide (10%)	—	—	—	2 ml
Water to make	1 liter	—	—	—
Time of development (68°F)	25 min	10 to 20	10 to 20	10 to 20
Exposure increase	3 to 4 times		2 times	

The oxidation products of *p*-phenylenediamine stain skin or clothing. This staining problem is minimized with the ortho compound, but *o*-phenylenediamine is not as active at low pH as the para derivative.[66,67] When combined with Metol, as in Windisch W 665, *o*-phenylenediamine produces fine-grain images with low densities in the negative highlights.[68] This formula (given in Table 5) with its compensating action to prevent high density formation is especially suitable for recording subject matter with excessive contrasts. About 30% less exposure than with Sease No. 3 is required for the Windisch W 665 development.

Metol, Glycin, and *p*-phenylenediamine were combined into a fine-grain developer by Harry Champlin.[69] Champlin No. 7 was a formulation that was of some interest in the mid-1930s when miniature cameras first achieved their popularity.

Film developed in the Champlin No. 7 formula required 50% more exposure than film developed in D-76. Champlin No. 7 also required a longer development time and produced slightly coarser grain than D-76.

Champlin No. 7

Water	1000 ml
Metol	2.5 g
Sodium sulfite	45.0 g
Benzoic acid	1.0 g
Salicylic acid	0.5 g
Boric acid	2.5 g
Glycin	11.5 g
p-Phenylenediamine (pure base)	11.5 g
Processing temperature	70 to 74°F

Paul Arnold[70] noted that "Some of the alchemistic additions that have been recommended to improve fine grain developers are astonishing in the sheer imagination, the untutored pioneering spirit they reveal."

The staining, toxicity, and slow-acting properties of *p*-phenylenediamine may be avoided, according to the British patent 466,625,[71–74] by combining *p*-phenylenediamine and a phenolic developing agent into a combined developer salt for use in low-alkalinity solutions. Meritol has been the name given to the *p*-phenylenediamine–catechol complex. Meritol may be used alone at 13.7 g with 90 g of sodium sulfite to yield one liter of a fine-grain developer, or 2.3 g of Metol may be added to this solution to increase the developer activity. An example of a more active version of a Meritol developer is the MCM-100 formulation given in Table 5.

The dialkyl-substituted *p*-phenylenediamines, so commonly used in color developers for color films, are more active than the unsubstituted *p*-phenylenediamines. G. W. Crawley[75] has compounded diethyl-*p*-phenylenediamine sulfate with hydroquinone or its chloro derivative to produce formulations suitable for modern films. These developing agents are thought to form addition compounds in solution that are superadditive in activity. The FX-9 formula which follows produces slightly more than normal emulsion speed in the 5- to 11-minute development time at 68°F. The FX-10 is a buffered borax version.

FX-9

Sodium sulfite (anhydrous)	100 g
Chlorohydroquinone	7.5 g
Diethyl-*p*-phenylenediamine sulfate	7.5 g
Water to make	1 liter

FX-10

Sodium sulfite (anhydrous)	100 g
Hydroquinone	6 g
Diethyl-*p*-phenylenediamine sulfate	6 g
Borax	4 g
Boric acid	4 g
Water to make	1 liter

PHYSICAL DEVELOPMENT

Physical development has been suggested as a processing technique to secure fine-grained silver images. In pure physical development the silver used to amplify the latent image is supplied from the developing solution, which contains a soluble silver salt, such as silver nitrate, and a developing agent. The developing agent reduces the silver ions to metallic silver, which deposits on the silver atoms of the latent image. Such a physical developer may be used to develop the latent image after the photographic material has been completely fixed (postfixation physical development), or before the silver halide has been removed (prefixation physical development). If the silver halide is still present, some silver ions from the crystals may be dissolved and used to reinforce the latent image. This action is the one used solely in low-pH physical developers containing *p*-phenylenediamine. This developing agent dissolves the silver ions from the silver halide, and then the reduced silver is deposited on the latent image, which serves as nuclei for a type of slow plating process that builds the latent image to a visible state.

Physical Development after Fixation

Pure physical development was the method of Louis Daguerre, who caused vaporized mercury atoms to coat the latent images formed from silver iodide. Fox Talbot used silver nitrate and gallic acid as a physical developer to develop the latent image in his Calotype process. Physical development with pyrogallol was used by Frederick Scott Archer with the wet collodion process, and William de W. Abney[76] appeared to be aware of the nature of physical deposition of silver on dry plates as early as 1878. Franz Kogelmann and R. Neuhauss[77] were investigating development after fixation before the turn of the century.

One method has been suggested by the Lumières and A. Seyewetz.[78] After the photographic material has been exposed about 10 times the normal

exposure, the material is fixed in the dark for 5 min in 30% sodium thiosulfate solution containing 10 ml of ammonia per liter of fixing solution. Washing for no longer than 1 hr is carried out by several changes of water made alkaline with ammonia. Both the fixing solution and the wash water are made alkaline to help minimize the attack of the thiosulfate upon the silver of the latent image. The fixed photographic material is developed for several hours by inspection in the light in the following solution, made by using five volumes of solution A mixed with one volume of solution B:

Solution A

Sodium sulfite (anhydrous)	180 g
Silver nitrate, 10% solution	75 ml
Water to make	1 liter

Solution B

Sodium sulfite (anhydrous)	20 g
p-Phenylenediamine (base)	20 g
Water to make	1 liter

Replace the solution each hour, as it is ineffective after that time.

A weak image, gray by reflected light and violet by transmitted light, was reported to have been obtained. A scum of metallic silver coating the emulsion surface must be carefully removed. Metallic silver is also deposited on the surface of the processing container. This deposited silver must be completely removed before processing is carried out in the same container again, as it may serve as competitive nuclei for silver deposition, thus limiting the degree of development of the latent image nuclei.

Henry Leffmann[79] failed in the use of this method, and others have reported a lack of success. The fixation of the silver halide crystals may result in the destruction of the latent image nuclei, although in some conditions it is possible that some deposition of silver from the thiosulfate complex may also help reinforce the latent image. E. R. Bullock[80] used a fixing bath of 18 g of anhydrous sodium sulfite in 100 ml of water, but this method of dissolving silver halide required many hours, even several days. A. and L. Lumière and A. Seyewetz[81,82] had found the solubility time for rapid plates to be too long for the use of sodium sulfite. G. Kornfeld[83] used thiosulfate plus 0.5% NaOH for fixation before development but found that the fixation was not uniform if the photographic material was vertical during the treatment.

Development after fixation, though possible, is difficult and erratic, and probably impossible with some modern dye-sensitized photographic materials of large grain size. Adsorbed sensitizing dyes to the atoms of silver of the latent image have been reported to interfere with the physical development process. The purity of all the chemicals used must be very high, as impurities may limit the silver deposition. The technique is critical: fixation times must be just adequate, but extended times will result in loss of some of the latent image. Washing must be complete or stains will result. The huge increases in exposure (up to 100 times normal), the long times of processing (often from six to 12 hr), and the fact that the silver particle size becomes more coarse when development is carried to the point where normal densities result, have limited this technique to the determined or the scientifically inclined.

Physical Development Before Fixation

Many of the disadvantages of development after fixation also apply to development before fixation, but the technique is less critical and the results more acceptable. One method that gained favor in the mid-1930s was proposed by A. F. Odell.[84–88] This method was claimed to require no additional exposure, but the results of P. K. Turner[89,90] or Bland H. Casebolt[91] would indicate that shadow detail would be lost without additional exposure. Franz Baur and Gottl. Imhof[92] found "that five- to ten-fold overexposure is necessary in order to secure the same threshold value that can be obtained with Metol hydrochinone." Two or more times the normal amount of exposure was said to suffice by Leslie B. Arey.[93] The physical development technique of Odell, however, was subject to difficulties, and various modifications were suggested.[94–98] The Odell method consisted of four steps: (1) immersion first in an iodizing bath, (2) development in a silver-containing solution, (3) fixation in an acid hardening fixing bath, and (4) washing and drying. The film is first immersed for 3 to 4 min in the following solution:

Forebath

Potassium iodide	5.0 g
Sodium sulfite, anhydrous	12.5 g
Water to make	500 ml

The treated film is rinsed in two changes in water, then developed for 25 to 30 min at 65°F in the physical developer, which is freshly made.

A concentrated stock solution is prepared from the following formulation:

Concentrated Silver Stock Solution

Sodium sulfite, anhydrous	50 g
Silver nitrate, crystals	8 g
Sodium thiosulfate, crystals	80 g
Water to make	500 ml

First dissolve the sulfite in 250 ml of water; then dissolve the silver nitrate in 200 ml more of water. Add the silver nitrate solution to the sodium sulfite solution and stir until all of the white precipitate is dissolved. Then add the sodium thiosulfate crystals with stirring until solution is complete, resulting in 500 ml of stock solution.

The concentrated silver stock solution is used then to prepare a one-time-use developing solution, which should be used within 10 min after mixing. This physical developer is prepared as follows:

Working Silver Developer

Concentrated silver stock solution	100 ml
Water to make	500 ml
Amidol (dry)	0.75 g

After a water rinse, then fixing, the surface of the photographic material should be swabbed to remove any silver scum on the surface before drying.

The instability and variability of the chemical baths, the long time of processing, and a considerable loss in emulsion speed of the film materials limited the use of the Odell physical developers to the mid 1930s when fine-grain development was needed to secure the best image quality from less-than-fine-grain photographic films in the 35mm size. Physical development has continued to be of research interest, however, through the years, particularly in efforts to secure a developing solution of greater stability.

Stabilizing the Activity of Physical Developers

In U. S. Patent 3,390,998 Roger M. Cole[99] described the stability of physical developers as follows:

Physical developers are inherently unstable, tend to darken and lose activity because of the interaction between the silver ion and the reducing agent present in the same solution. Means for increasing the stability of such solutions have been continually

sought. One method of increasing the stability has been to decrease the concentration of the reagents. This has led to solutions of very low capacity and to a very retarded rate of development. Solutions having high activity and high capacity tend to show sludging; that is, to form a dark precipitate which decreases the activity and usefulness of the physical developer.

Some improvement in the stability of physical developers is obtained by the addition of various ionic surfactants as described in Jonker et al., U. S. Patent 3,157,502 incorporated herein by reference. Such surfactants include amines, sulfonates, and the like. However, the resulting increase in stability is not enough to permit storage of the stabilized solutions for more than several hours and still maintain reasonably active development rate. Further development with such solutions becomes less selective as the solution is used: that is, silver is deposited not only on the image site, but also on background areas, container walls, rollers, etc., used in conjunction with the processing cycle.

Ionic surfactants increase the life of the developer about 50%, but nonionic surfactants are ineffective. Roger Cole claimed an additional 50% gain in useful life if organic compounds which form complexes with ionic silver were used in combination with the surfactants. Such organic silver-complexing compounds include cyclic amines, triazoles, thiazoles, tetrazoles, oxazoles, pyrimidines, and many other compounds, often containing the —SH group. These compounds have often been used as organic antifoggants. Hyamine 10X (Imperial Chem. Ind.) and cysteine were an effective combination when used in a physical developer of the formula

Part A (pH 11.0)

Water	800.0 ml
Sodium sulfite	20.0 g
Sodium isoascorbate monohydrate	20.0 g
Sodium carbonate monohydrate	50.0 g
Water to make	1.0 liter

Part B

Water	800.0 ml
Sodium thiosulfate pentahydrate	30.0 g
Silver chloride	7.2 g
Water to make	1.0 liter

to physically develop positive film that had been fixed, after exposure, in a solution containing sodium thiosulfate pentahydrate at 50 g/liter and sodium

carbonate monohydrate at 50 g/liter for 3 min, then rinsed 30 sec in water before treating for 10 min in the physical developer.

Similar stable sources of silver, such as silver thiazoline thiones or silver thiazolidine thiones, have been claimed[100] to be incorporable in the light-sensitive element consisting of a silver-sensitizing dye complex (made by reacting a cyanine sensitizing dye with silver nitrate). The stable sources of silver may be present in a physical developer for treating silver-dye radiation-sensitive materials.[101] An unusual copper developer has been proposed for physically developing the exposed silver-dye materials. A 20-sec immersion in a copper developer of the composition

Cupric nitrate	50 g
Ascorbic acid	40 g
2-Aminoethanol	100 ml
Sodium sulfite	50 g
Water to make	1 liter

produced a negative image of a maximum density that contained 99.7 mg of copper per square foot.

In this copper physical developer, according to John Williams and Paul Brewster Gilman,[102]

> The cupric nitrate can be replaced, if desired, by an equivalent amount of any other water-soluble cupric salt; e.g., cupric chloride, cupric bromide, cupric sulphate, cupric acetate, cupric benzoate or cupric lactate. The ascorbic acid functions to reduce the cupric salt to copper in the presence of latent image, and can be replaced, if desired, by sodium ascorbate. The 2-aminoethanol component acts to control the alkalinity and also functions as a complexing agent for the cupric salt. If desired, it can be replaced by any other water-soluble nitrogenous organic base such as any other aminoalkanol containing from 2 to 4 carbon atoms; e.g., propanolamine, butanolamine or diethanolamine; a primary, secondary or tertiary amine; e.g., methylamine, ethylamine, butylamine, diethylamine, triethylamine, piperidine or pyridine; an alkane diamine; e.g., ethylenediamine, 1,3-propanediamine, or 1,2-propanediamine; the sodium salt of ethylene diamine tetraacetic acid; or a sulphur dioxide-amine adduct; e.g., methylaminoethanol-SO_2 or methylaminopropanol-SO_2. The sodium sulphite component acts primarily as an antioxidant and can be substituted by an equivalent amount of another alkali metal sulphite; e.g., lithium sulphite or potassium sulphite, or with ammonium sulphite. However, it should be understood that the cupric salt and the reducing agent are essential components in the above formulation, and that the preferred combination is cupric nitrate and ascorbic acid.

Gelatin has been found[103] to increase the stability of a *p*-hydroxyphenylglycine physical developer "considerably," that is, up to 190 min at 20°C in a

quartz tank, in which stability was found to be 20 to 40% higher than in a glass tank. Exposed motion picture positive film was fixed for 45 sec, 20°C, in

Sodium thiosulfate pentahydrate	300 g
Sodium hydroxide	6 g
Distilled water to make	1 liter

(pH 10.0), then washed with distilled water for one hour. Physical development was carried out in a solution of

p-Hydroxyphenylglycine (purified)	0.005 *M*
Silver nitrate	0.025 *M*
Gelatin (purified)	0.5%
Sulfuric acid	0.5 *N*
Water to make	1.0 liter

The solution is used, immediately after preparation, in a tank that has been washed with hot concentrated nitric acid, tap water, and then distilled water.

THE TECHNIQUE OF SECURING FINE-GRAINED IMAGES

Producing a fine-grained photographic image is not the result solely of choosing a suitable developing solution, rather, it involves a train of events that must be optimized to achieve the desired result. The emulsion maker and coater start the cycle by selecting the size and distributing the silver halide crystals in the photographic material. When the emulsion manufacturer has striven to provide the best of the compromises that must be made to secure the most desirable emulsion sensitivity, tone rendition, and image contrast, the picture maker is faced with the task of maintaining the conditions that will not degrade the graininess given by the photographic material. (See Figure 5.)

The choice of the photographic material is critical to the fineness of grain to be achieved. The selection of a high-speed, coarse-grain photographic material will severely limit the fineness of grain particles that can be secured by any future solution treatment. The first decision the photographer makes in his quest for fine-grain photographic results is to always use the slowest-speed, finest-grain, photographic emulsions sufficient to achieve those results. But even a judicious decision does not insure the results. The exposure of the silver halide material, the ingredients of the developer and their concentration, the time and temperature of the developer solutions, and the

Figure 5. Although graininess destroys fine detail, grain can sometimes be used to advantage for pictorial effect. (Photograph by Grant Haist)

conditions of fixing, washing, and drying of the photographic material may still influence the graininess of the image.

Minimum usable exposure can help to minimize graininess in the final image. Minimum exposure will tend to confine the developable latent image nearest to the emulsion surface. As exposure is increased, the image will be found to extend into the depth of the emulsion. As it penetrates the emulsion layer, the exposing light tends to bounce off crystal surfaces, eventually being absorbed by crystals that are laterally displaced from the original direction of the impinging light. This effect, called irradiation, causes an image point to expose more crystals than are needed to record it. In addition, the image point is not recorded by a single grain, as the grains are microscopic in size, but by a large number of grains. Because irradiation increases the number of crystals used to record the image point, the developed silver image of that point will be the result of the massing of many filaments. The greater the number of silver particles together, the greater the possible nonhomogeneity of the silver image. The greater the depth of the image, the greater the likelihood that silver particles will overlap optically to produce nonuniformity of the silver deposit.

Any factor that causes the silver particles to be clustered together increases the appearance of nonuniformity. It is this lack of homogeneity of density that the human eye senses as graininess. Graininess is the visual impression of the nonuniformity of dark-colored metallic silver deposits adjacent to lesser amounts of metallic silver distributions in the photographic image. The eye cannot distinguish the silver particles, or even clusters of silver particles, as these are microscopic in size; it receives only a general impression of the minute areas that constitute the image. When these minute areas of dark silver and lighter adjacent areas become sufficiently separated so as to be detected by the eye, as in a photographic enlargement, the subjective impression of graininess is produced. Thus, magnification of the silver photographic image calls attention to its nonhomogeneity, which might not have been detected at all at lower magnifications.[104]

Early work by Loyd A. Jones and Noel Deisch[105] showed that graininess is most apparent in the highlights and lighter densities of the photographic print. They found that

> Anything that will tend to reduce the graininess in those densities of the negative from which these portions are printed will result in an effectively lower graininess in the result. As the gamma or the contrast of the negative increases, its higher densities tend more and more to take their position on the upper portions of the graininess-density curve; and since it is the higher densities from which the highlights and lighter tones of the print are taken, it is these densities which virtually determine the graininess of the print.

Exposure controls the density of the silver image on the negative or print; the degree of development determines the contrast of the developed silver image. Thus, minimum exposure and a low-contrast silver image both favor fineness of grain, resulting in a more uniform appearance of the image of the lower densities of the print where graininess is most objectionable.

Graininess is the subjective sensation in an observer in response to the nonhomogeneity of the image. The result of the instrumental evaluation of the properties of an image that produces the subjective sensation of graininess is called granularity. Such an instrumental measurement eliminates the subjectivity of human observers and provides numbers that can be used to compare objectively the graininess of different photographic materials. Root-mean-square granularity numbers are now increasingly used for comparing the graininess of photographic films. According to R. A. Morris and D. H. Wait,[106] "Root-mean-square (rms) granularity is a measure of the spatial variation of density which is obtained when numerous readings are made with a microdensitometer. The square *root* of the arithmetic *mean* of the *squares* of these readings is the RMS granularity value." Morris and Wait found that the relationship of granularity to graininess was dependent upon the contrast and the density level of the image and the characteristics of the measuring instrument. They summarized their findings as follows:

1. the graininess of a print, where contrast and sharpness are constant, varies directly with the granularity of the negative;
2. increasing the print film contrast increases the graininess of the print by amplification of the negative grain:
3. increasing print film sharpness increases graininess of the print by better resolution of the negative grain; and
4. printer characteristics, relating to contact, specularity, and other factors affecting sharpness and effective contrast significantly alter the observed graininess of prints.

A more contrasty picture appears more grainy than a less contrasty one. Daan Zwick[107] studied the quantitative relationship between contrast and granularity, finding that an 8% change in gamma caused a 6% change in granularity. Zwick[108] found a critical density at which graininess was most objectionable in projected still and motion pictures. According to Zwick, "This density is relatively invariant with screen luminance, since it is relative to the adaptive white level of the picture. For color pictures this diffuse density is 0.9, including base and stain. For black-and-white images, measured diffusely, the value is 0.64. The difference between monochrome and color is due mostly to the Callier Q factor of silver images. For television display these values are displaced to 1.03 and 0.83, respectively." If granularity measurements are made at only one density, then such measurements would

be most meaningful if they were made at or near the values listed where graininess becomes most objectionable.

Graininess has been observed for some time to depend upon the nature of the photographic image, being most evident in areas of uniform, moderate density. Just-noticeable differences in terms of rms granularity for different color image content were studied by Daan Zwick and Daniel L. Brothers, Jr.[109] For a uniform image field around 1.0 density a 6% change in rms granularity was detectable as a graininess difference. For an average picture a 16% change in rms granularity was a just-noticeable difference. When the scene is very complex with much detail, a 30% change in granularity is needed to produce a just-noticeable difference. These values also apply as well to still and motion pictures, and probably also to the display of film on television.

Graininess—or its objective correlate, rms granularity—has been found to depend upon the contrast of the image. Low image contrast may be achieved by low-pH developing solutions, usually containing weakly activated developing agents and often with considerable amounts of silver halide solvents. Short developing times, even with more active developers, produce images with finer grain. The silver halide solvent in the developer etches the crystals in the emulsion layer, reducing the crystal size and influencing the size and form of the silver filaments produced by development. Some of the silver dissolved from the crystals may be deposited on the silver filaments., thickening them. For this reason a strong solvent, such as thiocyanate, is probably less desirable than a milder one, such as sodium sulfite. Strong solvent action also means a greater loss of emulsion speed. In *p*-phenylenediamine fine-grain developers the developing agent acts as a mild solvent, producing low-contrast images of extremely finely divided physically developed silver. This is achieved at the expense of a great loss in emulsion speed.

Fine-grain developers are often slow acting. Jones and Deisch[105] found that graininess appears not to be a function of the speed of development but rather to be related to the properties of the alkali used to activate the developing agent so as to shorten the developing time. Some developing agents may be thought to be grain producing, but the grain may be produced by the nature of the alkali needed to secure even weak development. Some alkalis, such as sodium hydroxide, appear to have a disintegrating action on the gelatin of the emulsion layer. This action gives the silver particles a greater chance to come together to form clumps, thereby increasing graininess. Developing agents requiring the stronger alkalis may become associated with the production of grain, even though some of this may be due to the action of the alkali.

Only underdevelopment was found by Philip A. Friedell[110] to decrease the coarseness of the image structure over that existing in the original emulsion. He reported that developers containing thiocyanate or similar agents produced a coarsening of the image structure, even with underdevelopment. Apparently, physical developing action was sufficient to thicken the silver particles. Sodium sulfite functioned primarily as an accelerator and did not significantly decrease image grain. Bromides and iodides in the developing solution, like thiocyanates and other silver halide solvents, had a detrimental effect on the image structure, suggesting that fine-grain developers should be used only once, as these halide ions are produced during film processing. Monroe H. Sweet[111] has stated, however, that used developing solutions produce finer-grain results than the more active fresh developer, even after increased time of development for the used solution. Friedell concluded that fine grain depended solely on the degree of development—that is, the extent to which the silver has been reduced. The finest grain was produced, according to Friedell, "with a normal developer coupled with suitable overexposure of the film with development carried to a degree where a *negative printable on the hardest grades of paper only*, is produced." The use of contrasty paper for the print will emphasize graininess, so that some of the fine-grain characteristics of the negative may be lost.

A compromise must be made between the degreee of development or contrast of the film material and the degree of contrast of the photographic paper of the print. J. I. Crabtree[112] has said that it is better to develop a negative to a low gamma and make the print on contrasty paper than to produce a higher-contrast negative and make the print on softer paper. Because fine-grain development often involves the action of low-activity developers, these solutions are particularly sensitive to the effects of use: reduction of activity through exhaustion of the developing agents; the increasing restraint of the buildup of bromide and iodide in the solution resulting in a loss of shadow detail; and an accumulation of gelatin, dirt, and other foreign matter that may degrade the image upon enlargement. For these reasons a developer used once, then thrown away, is ideally suited for consistently maintaining the highest quality, fine-grain production.

Although the effect of processing conditions has not produced a consensus concerning the optimum film treatment, it is generally felt that the wet time of processing should be as short as possible. If the photographic material with the finest-grain emulsion is chosen, a more rapid-acting developer may be used, shortening the development time, and yet fine grain is achieved by the inherent characteristics of the photographic material. A 30- to 60-sec wash in running water rather than an acid stop bath is suggested to follow low-pH developers. A rapid fixing bath will speed up this time-consuming step to be followed by the minimum wash time. All processing solutions, including the

wash water, are at essentially the same temperature to minimize swelling variations of the emulsion layer in the various liquid baths. A few seconds treatment in a wetting solution should be followed by drying at room temperatures, but long-time drying under humid conditions should be avoided.[113]

The conditions most suitable for fine-grain development have been summarized in the preceding paragraph, but it should be noted that there is no absolute agreement between various investigators. Jones and Deisch failed to note any difference in image graininess when a pyrogallol developer was used at 15, 20, 25, or 30°C. The addition of considerable concentrations of potassium bromide to the pyrogallol developer failed to show any appreciable effect on the graininess of the strips, nor did the use of an acid fixing bath following the alkaline developer.

A. Marriage[114] reported the lack of effect of processing conditions upon image structure. Arthur C. Hardy and Loyd A. Jones[115] stated that "the fixing, washing and drying conditions were found to have no effect on graininess." The rate of drying had no effect in the studies of F. L. English.[116] As is often true in photographic processing, the individual processor often has to determine the validity of the prescribed recommendations to his own operating procedures and photographic materials.

Modern concepts of securing fine-grain development are based primarily on the nature of the photographic emulsion, with carefully selected grain size and grain distributions contained in thin, compact emulsion layers. R. B. Willcock[117] has said, "The solution of the fine grain problem will doubtless be found in newer emulsions, not in the rearrangement of old [developer] formulas; for that reason it is wisest to make the best of what we have available and wait." This was said in 1936.

For those of today's photographers who cannot wait any longer for the ultimate in fine-grained emulsions, possibly following Lloyd E. Varden's "Five Factors for Fine Grain" would be the best course:[118]

First—Select a film as slow and of the finest grain as the conditions of exposure and development permit.

Second—Expose the film properly but not more than is necessary to record the amount of shadow detail desired.

Third—Develop the film in a suitable fine-grain developer in which as much film speed as possible is assured.

Fourth—Develop the film to a gamma of about 0.7 [or less] as approximately indicated by time-temperature tables.

Fifth—After complete fixation and washing in solutions of the same temperature as the developer (preferably 65°F), dry the film normally in a warm current of dust-free air.

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Chapter 9
High Definition Developers

A high definition developer enhances chemically the edge effect between areas of adjacent tone, thus giving a visual sensation of higher definition.

JEREMY HAWORTH[115]

RESOLVING POWER

Definition in a photographic system has been defined as "the quality aspect of photographs that is associated with clarity of detail,"[1] a subjective impression made on the human mind from the overall visual appearance of the photograph. Definition is the result of many subjective factors, some of the more important being graininess, resolving power, sharpness, and tone reproduction. Thus, graininess, which was discussed in the last chapter, is only one of the factors that determines the quality of a photographic image. Developing solutions must be formulated to minimize the graininess of the final image but also to accentuate the other factors that lead to photographic images of high definition. Unfortunately, all the factors do not go hand in hand but may vary independently and be at odds with each other.

Resolving power, one factor influencing the rendition of detail, is the ability of the photographic material to separate closely spaced lines as viewed under magnification by an observer. The resolving power of a photographic image is usually expressed in terms of the maximum number of lines per millimeter that are just distinguishable. This means of evaluating image

quality was first studied by F. L. O. Wadsworth[2] in 1896 and has been used ever since as a means to evaluate photographic images.

Resolving power, noted C. E. K. Mees[3] in 1909, depends upon the irradiation arising in the emulsion layer, caused by the light scatter (reflection and diffraction of photons) of the exposing illumination. The light-scattering effect of the turbidity of the emulsion layer was also noted by W. Scheffer.[4] The turbidity of the medium depends upon the size, number, and optical constants of the particles distributed in it—in this case, silver halide crystals imbedded in gelatin. When very small, the particles do not diffuse the light to any great degree; as the particle size increases, the turbidity of the medium increases to a certain value, beyond which increases in particle size decrease turbidity. At a certain value of grain size, light scatter or irradiation reaches a maximum, resulting in exposure of silver halide crystals that will obscure the normally clear areas (unexposed) between lines of the resolution test pattern.

Resolving power is not influenced solely by light scattering, however, but was said by Scheffer to depend upon the following:

1. Intensity, direction, and colour of the light forming the image;
2. on the turbidity, gradation, colour (absorption), and spectral sensitiveness of the film, on the size of the light-sensitive particles, and on the size and relative positions of the developed grains to these latter;
3. on the manner of development; and
4. on the after-treatment.

Unwanted exposure at the edge of image details results in a loss of edge contrast, making it difficult to distinguish between fine lines that are close together. Increased exposure increases the amount of irradiation, because more light photons are available for scatter through more depth of the emulsion layer. Increased exposure also increases the possibility of halation, the reflection of some of the exposing light from the rear surface of the emulsion or the support. Irradiation within the emulsion layer may be limited by putting a light-absorbing dye in the layer. Halation is suppressed by coating a light-absorbing layer directly under the emulsion layer (antihalation undercoat), or the light-absorbing layer may be on the back of the film or plates. In some cases, the base material may contain a light absorber, such as in gray-base 35mm films. (See Figure 1.)

Halation effects in modern film materials are not as evident as the halos produced by unbacked glass plates of the past, but both halation and irradiation are evident when leafless tree branches are photographed as a silhouette against a bright sky. The tracery of the fine branches may be obscured by exposure from scattered or reflected light that causes development to occur in these fine details that should remain without developed silver.

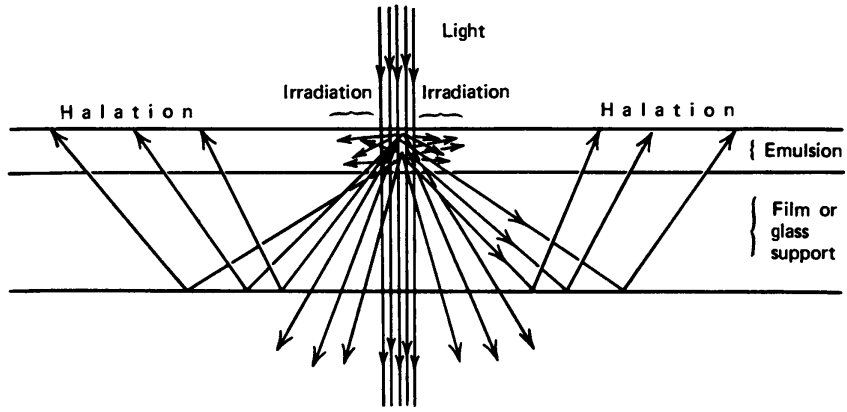


Figure 1. The exposing light, impinging on the emulsion layer, is scattered by the particles in the emulsion and may be reflected from the film or glass support. [*Leica News*, No. 33: p. 68 (1938)]

Resolving power would appear to be a logical and simple quantity to measure to characterize a photographic material. In practice, however, a meaningful quantitative evaluation has been difficult to achieve. The measured values depend upon the ratio of the line to the width of the space between lines and upon the contrast in the object photographed for the resolution test.[5,6] High-contrast test objects give different resolution values than low-contrast ones. The color temperature of the light or the wavelength of monochromatic radiation used for the exposure is also a factor in the results. Instrumental evaluation of resolving-power exposures may resolve fine detail that the eye does not perceive and use to evaluate an image.[7] Some camera lenses have been found that do not yield their maximum resolving power when focused to provide an image of maximum sharpness such as would be the case in actual visual focusing, but provide maximum resolving-power values when slightly out of visual focus.[8,9]

Resolution is not a definite property of a photographic emulsion, being very sensitive to the time of exposure; both over- and underexposure are detrimental. The treatment of light-sensitive material in a photographic process is also a factor. Kenneth Huse[10] has found that "If two plates of the same emulsion, exposed equally and under the same conditions, are developed in different developers, the values of resolving power obtained vary widely, the greatest deviation from the maximum value being of the order of forty percent with the developers tested." Another investigator, P. Hariharan,[11] found peak resolution to vary only slightly with the degree of development. Increasing development time did cause the exposure corresponding to the peak resolution to decrease. However, Fred H. Perrin and

J. H. Altman[12] found that "Except for a certain thiocyanate developer, all the developers studied gave substantially the same resolving power for practical gammas or image contrasts."

Resolving power is an attribute of definition in a photographic image, but because it is influenced by so many factors, simple measurements are unable to provide a fundamental relationship that is consistently meaningful. Neither the resolving-power values derived from high-contrast objects nor those from low-contrast objects are a unique measure of definition.[13] Not only resolving power but also graininess, sharpness, and tone reproduction are involved in an observer's impression of the clarity of detail of a photographic image. Sharpness is thought to be the major determinant, however. Unfortunately, sharpness is another subjective concept, the impression received by an observer when viewing an image containing the boundaries of clearly resolved elements of detail.

IMAGE SHARPNESS

The sharpness of photographic materials, according to R. E. Stapleton,[14] is affected by two factors—the grain size of the developed image and the image diffusion or image spreading caused by the scatter of the exposing light. Image diffusion may be modified by development effects occurring between adjacent developing areas. The structure of the developed silver image depends upon graininess resulting from the dispersion of the metallic silver particles from development.

Individual silver particles would not be a factor in image graininess even at great magnification, as the individual particles are much too small to be resolved. In image areas of uniform, intermediate density the distribution of the silver particles may produce the mottled appearance—graininess—that becomes objectionable to the eye. According to Philip A. Friedell,[15] spherical areas caused by air bubbles, devoid of silver halide, in the emulsion layer also contribute to the grainy appearance of the image. At a suitable magnification, this nonhomogeneous nature of the particulate image caused image definition to deteriorate, resulting in a loss of image sharpness. However, air bubbles in a coating, or even holes where the silver halide grains have been fixed out, are usually thought to have a small effect as compared to that of light scatter.

The image of a sharp edge is affected by the scatter of the exposing light, ranging from a few microns in the finest-grained layers of low turbidity up to nearly 0.1 mm for a heavy exposure in a high-scattering emulsion layer (according to Stapleton). The results of the more gross effects may be detected by the eye at lower magnifications than are needed to perceive the graininess

of the image. Light scatter depends on the color of the exposing light as well as the size, number, and separation of the silver halide crystals of the photographic material.

Sharpness is the impression a human being gets when observing the detail in a photographic image. This impression is the result of studying the transition of the density of the image at the boundary of a light and a dark area. When photographic materials are given knife-edge exposures—that is, one area of the photographic material protected from the light, the adjacent area unprotected—the image density does not drop to zero in the protected area, but the density gradually decreases from the edge boundary into the area shielded during exposure. This encroachment of the light by reflection, refraction, diffraction, and scattering represents a loss of light from the edge of the exposed area. The diffuseness of the edge boundary is less with fine-grained photographic materials of low turbidity than with coarse-grained materials of high turbidity. (See Figure 2.)

In 1953 G. C. Higgins and L. A. Jones[8] proposed to measure instrumentally the diffuseness of the edge boundary of a knife-edge exposure and use this as an objective measure of sharpness. A microdensitometer, an instrument capable of recording the density, or degree of blackness, of very minute areas, was used to scan across the boundary of the knife-edge image. It was hoped that a maximum change in density from the exposed to the unexposed area, or the maximum gradient recorded by the microdensitometer profile of the density variation at the boundary, could be a measure of the image sharpness of various film materials. This, however, was found to be untrue.[16]

When viewing the edge of a photographic image, the human eye scans back and forth across the edge at about 50 to 100 times per second. The cones of the eye respond to the suddenness of the change in the illumination from the edge being scanned. Jones and Higgins[17] derived a mathematical definition of sharpness called acutance that involved both the gradient of the change in density across the knife-edge image and the total density difference between the dense and clear parts of the negative.

Acutance, the objective correlate of sharpness, was compared with the results obtained by 20 observers ranking the sharpness of 10 different negative materials. All materials were ranked and spaced the same on the acutance scale as they were on the subjective sharpness rating scale. Acutance, however, did not correlate well with resolving-power measurements, just as sharpness did not correlate with resolving power. Higgins and Wolfe[1] reported that "When graininess and tone reproduction are constant and resolving power is adequate to reproduce all the detail that can be observed under the conditions of viewing, acutance correlates well with definition. On the other hand, when the resolving power is not adequate to reproduce all the detail that can be observed, it is also an important determinant of definition."

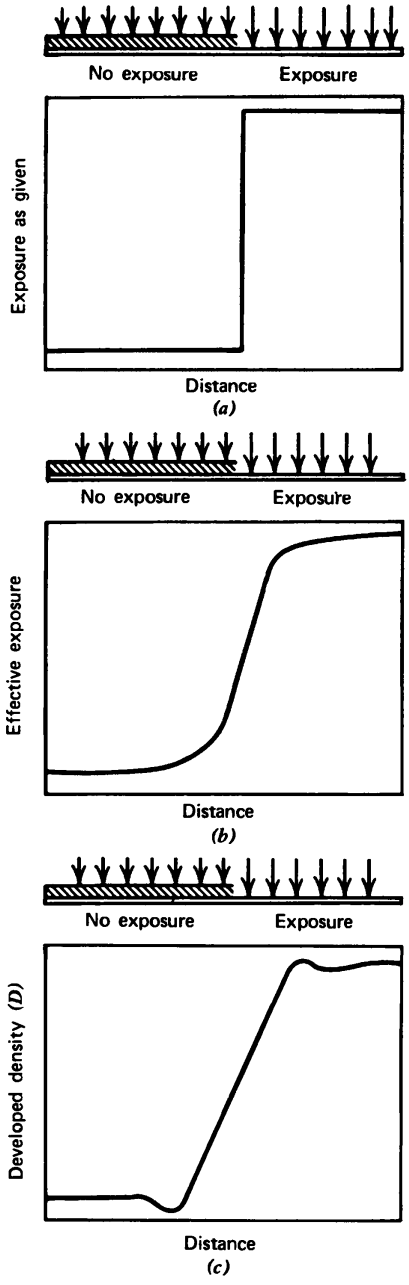


Figure 2. (*a*) Exposure as given represents sharply defined areas of exposure and no exposure in the emulsion layer. (*b*) Scattering of the exposing light across the boundary between exposure and no exposure makes the differences in exposure between these areas. (*c*) The developed density may exhibit edge effects that increase the density in the dense areas and decrease the density in the less dense areas.

Although more complex methods are now used to appraise the total performance of the various elements in a photographic system as described by Perrin[7] or Higgins,[18] the concept of edge sharpness has been valuable in the formulation of developers. The responses of various film products may be rated for a given developer, time of development, and color of the exposing light.[19] Even the more recent measurements of the modulation transfer characteristics of the emulsion, the effect on the microstructure of the image as a result of diffusion of light within the emulsion layer, are subject to modification to some extent by development edge effects.[17]

DEVELOPER EDGE EFFECTS

Photographic definition is influenced by uneven development effects that occur at the boundaries of image detail. These development edge effects, often called adjacency effects, can cause irregular changes in the size, shape, or density of the photographic image, especially observable at the boundary between areas of high and low development.[20] Adjacency effects are caused by local chemical changes in the developer occurring during the development period, and they may either enhance or restrain the amount of the silver image that would normally be formed.

Certain development effects have long been associated with unsuitable agitation of the solution during development.[21–25] When photographic film is oriented vertically during development, or the film is pulled through the solution as in a continuous processing machine, white streaks may appear near areas that contain considerably more image than adjacent areas. Black streaks may form below an area of low image development. Lack of agitation will cause uneven image development. According to E. R. Bullock,[26] "In ordinary development with vertical immersion and without agitation a downward current prevails, and the degree of development is accordingly somewhat greater near the top than near the bottom of the negatives; under usual conditions the density difference due to this cause is of the order of 5 percent or 10 percent." (See Figure 3.)

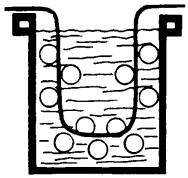
Light streaks on the negative, usually extending downward from a vertically developed image, or following after a developed area that has been machine processed,[27–31] are called bromide streaks. These streaks are the result of the restraint of development produced by the release of bromide ions, iodide ions, dyes, or organic restrainers from those areas of the emulsion where a high degree of development is occurring. These inhibitors of development, being added to the developer and increasing its weight over the surrounding solution, tend to trail from areas of high development, producing less image formation than the surrounding developer of normal composition. Such restraint of image formation is minimized by adequate agitation to

Figure 3. The sheet film negative of the Smithsonian Institution was developed vertically in a tank. The sky area was at the bottom of the vertical film. Unused developer from the silhouetted towers (very little exposure) moved into the nearby exposed sky area, causing increased development. This increased negative development resulted in the light streamers visible on the print from this negative. (Photograph by Grant Haist)

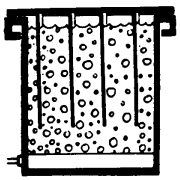
sweep away these unwanted products of development. The most efficient agitation involves swabbing the surface with a brush, sweeping the surface with a reciprocating paddle, or using a jet of liquid or bursts of rising gas bubbles.[32–35]

A developer effect may also produce dark streaks on the negative. Active, unused developing solution from an area of low or no development may diffuse to an adjacent area of high exposure, resulting in an increased reduction of silver there. Generally, under conditions of low agitation, the developer in an area of high exposure will be exhausted rapidly, releasing development-restraining by-products, so that the diffusing fresh developer will cause an increase in the rate of development over that which normally would have occurred. Agitation may be provided in a number of ways, as shown by Figure 4.[35]

BATCH PROCESSORS



Wringer roller: Film is transported and squeegeed by a sequence of rollers. **Strong points:** Vigorous agitation, automatic, repeatable, small volume of solution. **Weak points:** Large capital investment, may be limited in choice of chemicals, special problems in specific machines.

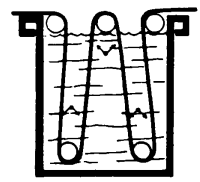


Nitrogen burst: Film stationary in solution. Agitation is provided by rising gas bubbles. **Strong points:** Random agitation at fairly high level, no moving parts. **Weak points:** Sensitive in design and operation to avoid patterns, possibility of adherence of bubbles to film, short development times a problem.

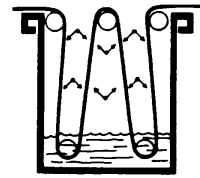
Manual lift and drain: Film is lifted out of the developer, allowed to drain, then returned. **Strong points:** Low capital investment, simple design. **Weak points:** High labor cost, low level of agitation, problem of streaks, operator variability.

Machine lift and drain: Similar to manual except lifting is done mechanically. **Strong points:** Semiautomatic. **Weak points:** Very low level of agitation.

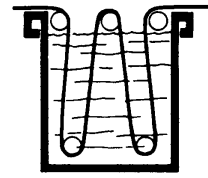
CONTINUOUS PROCESSORS



Immersion plus jet or spray: Film moving through solution provides some agitation with a jet assist. **Strong points:** Very vigorous and effective agitation. **Weak points:** Costly in installation, power requirements and maintenance.

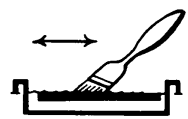


Spray: Liquid spray directed onto film as it passes through the tank. **Strong points:** Vigorous and uniform agitation, small volume of solution. **Weak points:** Sensitive design, developer oxidation.



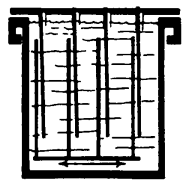
Immersion: Film moving through solution provides its own weak agitation. **Strong points:** Relatively inexpensive. **Weak points:** Streaks, weak agitation.

SMALL – VOLUME PROCESSING



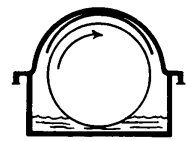
Brush: Film is laid flat in a tray and a soft brush is used to literally sweep it. **Strong points:** Very vigorous and uniform within a sheet, stagnant layer minimized. **Weak points:** Tedious, requires operator skill to minimize variability from sheet to sheet.

ASA tray: Film lies flat and rigid in bottom of a tray and is agitated by rocking the tray. **Strong points:** Vigorous, random agitation, no special equipment. **Weak points:** Tedious, requires operator skill.



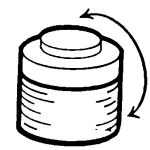
Vane: Blades in very close proximity to the emulsion surface sweep emulsion. **Strong points:** Good agitation if well designed, eliminates operator variability. **Weak points:** Very sensitive to small design changes and film flatness, expensive.

Tray shuffling: Sheets of film are shuffled in tray. **Strong points:** Fair to good agitation, no special equipment. **Weak points:** Possibility of damage to film, requires operator skill.



Drum processor: A single sheet of film or paper is attached to a blanket drum that kisses the developer solution as it rotates, bringing developer to print. **Strong points:** Excellent agitation, small amount of solution. **Weak points:** One-at-a-time operation.

Reel tank and spindle: Film is wound on a reel and rotated for agitation. **Strong points:** Easily executed, satisfactory for amateur. **Weak points:** Low level of agitation, directional effects (streaks).



Reel tank: Film is wound on a reel and tank rocked or shaken. **Strong points:** Fair to good agitation. **Weak points:** Not completely uniform.

Figure 4. Some methods of agitation during development. [Richard D. Zakia and Hollis N. Todd, *PMI* (*Photo Methods for Industry*), 8 (6): 33 (1965)] Reprinted from Photomethods Magazine. Copyright © 1965 Ziff-Davis Publishing Company.

Figure 5. Edge effects from development are not usually visible, but their presence on dark prints can sometimes be detected as a white line surrounding very dark areas. (Photograph by Grant Haist)

Development streaks of either greater or lesser density are undesirable, but increases of density on the edges of detail caused by development effects may sometimes be beneficial. This density increase, occurring to the greatest extent at the dense side of the boundary between areas of different degrees of development, has been called the "border effect." The restraint of development at the light side of the same boundary is called the "fringe effect." In most cases, border and fringe effects occur on the same negative, although the fringe effect may be difficult to detect in areas of low development. Generally, these effects are not perceptible except by microdensitometry, although enlargements on photographic paper or projection of the image may indicate their existence. (See Figure 5.)

Bromide and developer streaking are usually gross in character, easily visible at a glance; both are believed to be caused by the flow of the liquid developer over the surface of the emulsion layer. The fringe and border effects, usually not visible, are caused by diffusion of restrainers or fresh developer within the emulsion layer or in the thin, stagnant layer of liquid at the emulsion surface. In a photographic film containing a heavily exposed area next to a lightly exposed area, moderate agitation may be sufficient to prevent bromide and developer streaking but not the border and fringe effects. Bromide and other development restrainers from the heavily exposed area will diffuse from the edge of the developing area. Fresh, unused developer

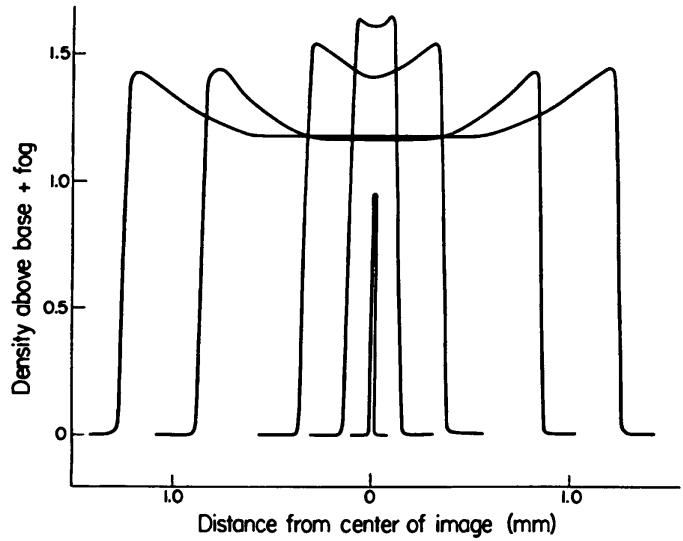


Figure 6. Eberhard effect is the dependence of density on image size. (L. J. Fortmiller, Eastman Kodak Company)

from the adjacent clear area will diffuse into the exposed area, producing the greatest increase of density at the very edge. The development increase produces less density as the distance increases into the dense area. The name "Mackie line" is often given to the white line that may surround dark objects in photographic images.[36–41]

Another development effect, the Eberhard effect, named after Gustav Eberhard,[42–47] is a special case of the border effect. Eberhard found that in many cases the density of the developed image was related to its size. Small images were found to have higher densities than large ones, even though both areas had the same exposure and development. In images of small area the image enhancement of the border effect extends across the entire image width. In fine detail on a negative the border effect causes the final density to be higher for small detail than it would be without the effect, thus improving the negative's acutance. (See Figure 6.)

HIGH-DEFINITION DEVELOPERS

The border and fringe effects increase the density difference at the boundary between image detail of different exposure. Fine line detail is enhanced by the Eberhard effect. In very recent years efforts have been made to compound developers that use these edge effects beneficially to give increased edge contrast to yield improved image definition. Such developer compositions are used with thin-layer, fine-grained photographic films of low or moderate speed. The thin emulsion layer limits the amount of light scatter for a point that occurs as a cone of light focused with the point at the surface of the photographic emulsion. Fine-grained emulsions provide the low graininess suitable for images of high definition and do this without the need for a developer that promotes fine-grain development by the use of solvents or underdevelopment.

Fine-grain developers may achieve the desired result, but the detail of the image may have diffuse or fuzzy edges. Harold Harvey[48] has noted that with *p*-phenylenediamine developers "Despite their fineness of grain, the images had extremely poor resolving power. Micro examination of many films revealed the fact that image areas were softened, those of dark areas against light not holding a sharp boundary. I at first ascribed this to irradiation, but subsequent work led me to believe that it is a characteristic of all *p*-phenylenediamine developers." Willi Beutler[49] found that any developer containing a high concentration of a silver halide solvent will give unsharp negatives with a loss of fine shadow detail near the emulsion surface. Even the quantity of sodium sulfite should not be greater than necessary to act as a developer preservative.

The importance of increased edge contrast has been recognized as a primary requirement for high-resolution development. Geoffrey Crawley[50] has pointed out that

> If print definition is to be good, then the contrast of fine detail in the negative must be good. Negatives are printed in an enlarger, and as is well known, light-scatter is produced in the negative as the beam of light from the enlarging lamp passes through it, producing a kind of flare. Flare reduces contrast, and thus the more flare there is, the less contrast of fine detail will tend to be when projected on to the printing paper.
>
> Hence, a negative which has a weak silver grain structure may be inclined to give softer print detail than one with a stronger structure. What produces a weak grain structure?—a fine-grain developer for one thing. Hence, we have two types of developer commonly used: the maximum or high-definition type, which is designed to produce a 'stronger' grain structure, even if it results in a slightly less fine-grained print in order that brilliantly crisp print outlines and detail can be obtained; the second type of developer in common use is the fine-grain developer, with its solvent action on the silver bromide crystals in the emulsion which assists the silver grains formed by the action of the developer to avoid clumping into coarse-grain structures giving a grainy print. This type definitely gives a finer grain, which can be essential with fast films or on some medium-speed ones when very big enlargements are to be made. The flare effect in the grain structure will also give a softer-looking print overall—not so vigorous that is, quite apart from questions of definition and sharpness. Between the two developer types there will sometimes be no great difference in resolution, but the better contrast of detail given by the maximum definition type will probably make the viewer think that resolution is better.

The use of fine-grain developers yields fine grain with a loss in sharpness of the image; the developer designed to utilize edge effects to increase image definition does so at the expense of increasing the graininess of the image. The possibility of providing developers that improve both the graininess and sharpness was the objective of a study by J. H. Altman and R. W. Henn.[51] They compounded two sets of developers: (1) fine-grain developers based on Kodak Developer D-25 with constant Elon concentration but with increasing amounts of sulfite ion and (2) high-definition developers containing low sulfite and a low Metol concentration such as was suggested by Beutler. The exact composition of these two series of developers is shown in Table 1.

In the fine-grain series of developers, as the sulfite concentration was increased, speed and granularity decreased as the rate of solution of the silver halide was known to increase. When the rate of silver halide solution reached a maximum and then began to decrease, the speed and granularity increased in a fashion to suggest a more-than-accidental relationship. With a constant sulfite concentration and thus constant solvent action, reducing the Metol concentration resulted in an increase in acutance without a serious loss of speed except for a high-speed film such as Kodak Tri-X film. Granularity, however, increased for a fine-grain film such as Kodak Panatomic-X.

Table 1. Constituents of Developers

Series	Formula No.	Kodak Elon (g/liter)	Sodium Sulfite (anhydr.) (g/liter)	Sodium Bisulfite (g/liter)	Total Sulfite (M/liter)	Kodalk (g/liter)
I (Fine-grain)	AH-1	7.50	10	0	0.08	4
	AH-2	7.50	30	5	0.29	0
	AH-3	7.50	100	15	0.95	0
	AH-4	7.50	200	20	1.80	0
II (High sharpness)	AH-15	2.50	10	0	0.80	4
	AH-16	1.00	10	0	0.08	6
	AH-17	0.50	10	0	0.08	20
	AH-18	0.25	10	0	0.08	20

Acutance continued to increase to the lowest concentration of the Metol which was tried. These results, as given by Altman and Henn,[51] are summarized by Tables 2 and 3.

Fine-grain development and high-sharpness development are not possible with the same solution. Results vary from one emulsion type to another, making generalizations impossible, some emulsions giving a more beneficial balance of results than others. A compromise must be made to secure the best speed-graininess-acutance relationship. Altman and Henn observed that "variations in Elon and sulfite concentrations have resulted in very much greater changes in granularity than in acutance." This is why the fine-grain developers (Series I) appear in general to be advantageous on a basis considering both graininess and acutance.

A high price must be paid in granularity by the high-sharpness developer in order to achieve a moderate gain in acutance. The gain in sharpness may be worth while, however, if the system is not grain-limited by the film emulsion. The fine-grain developer achieves its improvement in image structure but results in a loss of emulsion speed. This loss, in some measure, tends to offset the gain in acutance, with increased granularity, of the high-definition developer that requires no exposure increase. Thus, there is no clear-cut advantage for either the fine-grain or the high-sharpness developer, but the choice must be determined by the individual requirements of the film user.

Formulas for High-Definition Developers

High-definition developers are usually used with thin-layer, fine-grain photographic films of low or moderate speed. These films tend to produce

Table 2. Effect of Developer on Structure of Images: Speed, Acutance, and Granularity of Kodak Panatomic-X Film[a]

Series	Formula No.	Kodak Elon	Sulfite (g/liter)	Dev. Time (min)	Contrast	Speed		Acutance		Granularity	
					γ		%		%		%
I (Fine grain)	AH-1[b]	7.50	10	9	0.62	130	113	2340	106	0.027	123
	AH-2	7.50	30	8	0.63	125	108	2200	100	0.019	86
	AH-3	7.50	100	$8\frac{1}{4}$	0.63	82	71	2200	100	0.011	50
	AH-4	7.50	200	11	0.63	96	83	1850	84	0.012	55
II (High sharpness)	AH-1[d]	7.50	10	9	0.62	130	113	2340	106	0.027	123
	AH-15	2.50	10	4	0.61	107	93	2500	113	0.034	155
	AH-16	1.00	10	5	0.61	117	102	2550	116	0.036	164
	AH-17	0.50	10	7	0.69	129	112	2750	125	0.036	164
	AH-18	0.25	10	13	0.64	150	130	3100	141	0.034	155
Kodak Developer D-76 (1:1)[c]				$6\frac{1}{2}$	0.62	115	100	2200	100	0.022	100

[a] All data from single runs except as noted.
[b] Average of five runs.
[c] Average of two runs.
[d] Data repeated for convenience.

Table 3. Effect of Developer on Structure of Images: Speed, Acutance, and Granularity of Kodak Tri-X Film[a]

Series	Formula No.	Kodak Elon	Sulfite (g/liter)	Dev. Time (min)	Contrast	Speed		Acutance		Granularity	
					γ		%		%		%
I (Fine grain)	AH-1[b]	7.50	10	22	0.62	1090	128	950	79	0.074	132
	AH-2	7.50	30	20	0.67	910	107	1150	96	0.064	114
	AH-3	7.50	100	16	0.65	590	70	700	58	0.050	89
	AH-4	7.50	200	20	0.64	525	62	500	42	0.050	89
II (High sharpness)	AH-1[d]	7.50	10	22	0.62	1090	128	950	79	0.074	132
	AH-15	2.50	10	11	0.62	852	100	900	75	0.082	147
	AH-16	1.00	10	$11\frac{1}{2}$	0.62	795	94	900	75	0.084	150
	AH-17	0.50	10	26	0.67	795	94	1050	88	0.086	154
	AH-18	0.25	10	35	0.62	742	87	1150	96	0.090	161
Kodak Developer D-76[c]				$8\frac{1}{2}$	0.63	850	100	1200	100	0.056	100

[a] All data from single runs except as noted.
[b] Average of five runs.
[c] Average of two runs.
[d] Data repeated for convenience.

contrast easily, often excessively. A soft-working developing agent, usually Metol or Phenidone, will yield acceptable contrast and a good tonal scale in a suitable developing composition. A Metol-only developer produces a greater increase in the density of fine image detail than does a Metol-hydroquinone developer. The concentration of the developing agent or agents is very low, insuring that the developing agent will be exhausted rapidly in the heavily exposed areas of the film. The activity of the developing action is maintained by adequate alkali content to prevent losses in emulsion speed. However, it may be presumed that in areas of highly active development, the pH of the local developer may drop to a lower value. This local loss in pH would have a compensating action in itself, meaning the highly exposed areas would tend to develop at a slightly slower rate than if the solution had been highly buffered.

All conditions of development of the high-definition developer favor the formation of image edge effects. The exhaustion of the developing agent or the loss of activity caused by the formation of acid products during development restrain development in the areas of high exposure. Active developer diffusing from areas of low to high exposure will cause increased development of the boundary of the image, producing increased contour density but also increasing the size of the silver grains in the enhanced edge density. Because the high-definition developer must be carefully balanced chemically and used in dilute form, the solution is used only once, then discarded. This working solution is often prepared from a concentrated form of the developer or by mixing two solutions just before use. In some cases, conventional fine-grain developers, such as Kodak Developer D-76, are diluted with water to form the dilute developing solution that gives increased image edge effects, resulting in increased acutance values for the image.

HIGH-ACUTANCE DEVELOPERS

Typical high-definition one-use developers are those of Beutler (below) and Crawley (Table 4).

Beutler Formula[49]

Solution A:	Water	1000 ml	*Solution B:*	Water	1000 ml
	Metol	10 g		Sodium carbonate (anhydrous)	50 g
	Sodium sulfite	50 g			

Add 50 ml solution A and 50 ml solution B in turn to 500 ml water. Development: 7 to 10 min, 65°F.

Table 4. Crawley FX Acutance Developers[54]

FX-1 High-Acutance Developer (working solution)		FX-2 Acutance Developer (working solution)		FX-13 Acutance Developer (working solution)	
Metol	0.5 g	Metol	0.25 g	Metol	0.5 g
Sodium sulfite (anhydrous)	5.0 g	Sodium sulfite (anhydrous)	3.5 g	Sodium sulfite (anhydrous)	45.0 g
Sodium carbonate (anhydrous)	2.5 g	Glycin	0.75 g	Glycin	2.5 g
Potassium iodide (0.001% solution)	5 ml	Potassium carbonate	7.5 g	Potassium iodide (0.001% solution)	5 ml
Water to make	1000 ml	Pinakryptol yellow (1:2000 solution)	3.5 ml	Water to make	1000 ml
		Water to make	1000 ml		
(Speed increase : ½ to 1 stop)		(Speed increase: 80%)		(Speed increase: ½ stop)	

Developing time: approximately 12 to 18 min, 68°F, for FX-1 and FX-2. For FX-13, use times about two-thirds those given for FX-1 and FX-2. Use FX-13 only with slow-speed films. Faster film materials may show grain and definition disadvantages.

A modification of the Beutler formula has been suggested by Arthur Kramer.[52] Potassium iodide was added to increase the surface action and promote edge effects. Add one part of solution A, one part of solution B, and eight parts of water. For each liter of this solution add 2.5 ml of a 0.001% solution of potassium iodide. Kodak Plus-X film was processed for 10 min at 68°F.

Another modification has been suggested for the popular Beutler formula.[53] To 150 ml of Beutler solution A (use only the A solution), 21.2 g of sodium sulfite and 8.5 g of sodium chloride were added. The solution was made to a volume of 300 ml by adding water. A 9-min, 68°F development was proposed for Ilford FP3 film.

COMPENSATING DEVELOPERS

For subjects with great lighting contrasts, special techniques are used: modulation of exposure is combined with a special developing solution to provide optimum reproduction of subjects that are incapable of adequate rendition with normal developers. (See Figure 7.) Exposure is often based on the shadow readings to insure satisfactory detail rendering, then the negative is developed in a dilute developing solution of low buffering capacity. In the areas of highest exposure the developing agent is quickly exhausted, but the shadow portions of the negative continue to develop. Edge effects also are produced. The developing solution produces less density than normally would result in the high-exposure areas, that is, the developer compensates for the high exposures to produce a usable negative. Such compensation is quite striking: the classic demonstration involves photographing a lighted clear glass light bulb against the page of a book. A compensating developer produces a negative that shows the sharply defined filament with the letters of the printed matter clearly readable.

Hans Windisch[55] proposed such a compensating developer for extreme lighting contrasts:

Windisch Catechol Compensating Developer

Solution A:	Water (boiled)	100 ml	*Solution B:*	Water	100 ml
	Catechol	8 g		Sodium hydroxide	10 g
	Sodium sulfite (crystals)	2.5 g			

Tank development: 500 ml water + 12 ml solution A + 7 ml solution B. Development for 15 to 20 min, 68°F. Agitate "thoroughly" during development.

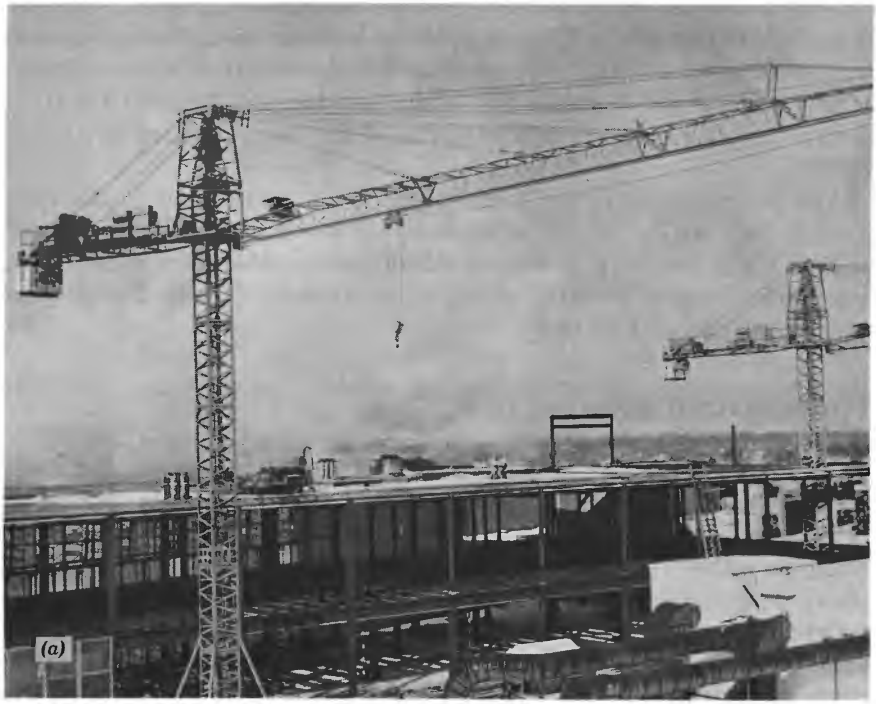


Figure 7. A compensating film developer produces negatives that yield prints with increased shadow detail. The negative for photograph (*a*) was given recommended development in a commercial Metol–sodium sulfite developer; the negative for photograph (*b*) was developed in a compensating pyrogallol developer. In the original prints, more shadow detail and better line rendition (the cables at the top of the crane, for example) are evident in the print from the negative developed in the compensating developer. (James King, Eastman Kodak Comapny)

A technique involving exposure control and development compensation was proposed by Willi Beutler to bridge great lighting contrasts.[56] Exposure readings are taken of highlight and shadow to establish the luminance range. The shadow readings are then increased by a factor that is related to the luminance range.

Luminance Ranges	Exposure Factors	Development Times*
1:25 to 1:100	2×	12 min, 65°F
1:100 to 1:300	3×	10 min, 65°F
1:300 to 1:500	4×	8 min, 65°F

* Applies to medium-speed panchromatic film. Add 2 min for high-speed film.

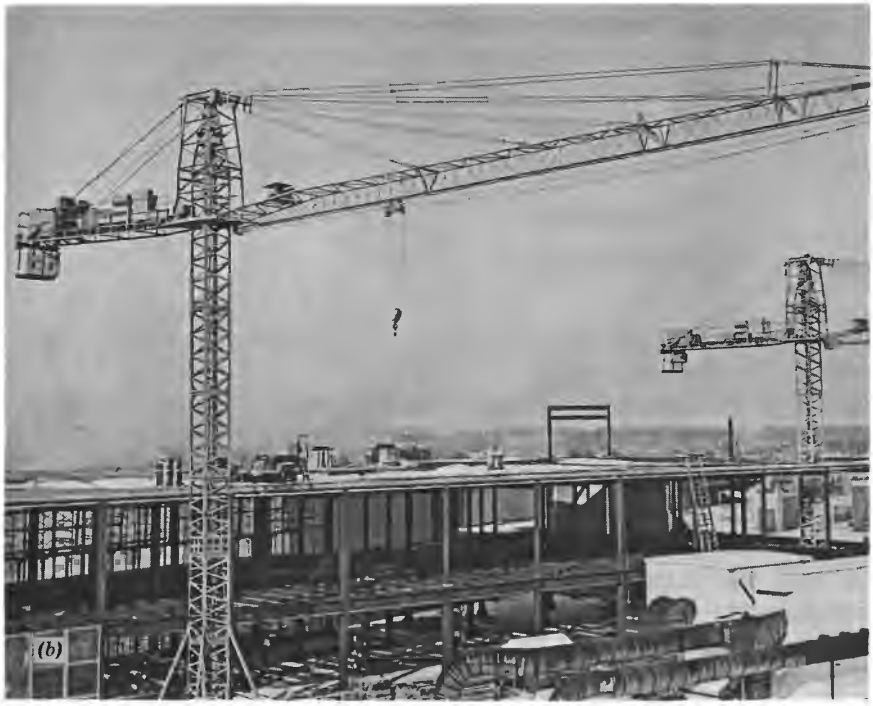


Figure 7. ***(continued)***

The developer is made as a stock solution:

Metol	10 g
Sodium sulfite, anhydrous	50 g
Water to make	1 liter

One part of the above solution is mixed with four parts of water to make the working solution. An acetic acid stop bath is suggested for strongly overexposed negatives to stop development quickly.

The superadditivity of Phenidone-pyrogallol developers was studied by Marilyn Levy.[57] A new compensating developer based on these findings was proposed by Silom Horwitz[58] and is shown on the following page:

Negative Developer D-512 (Horwitz)

Calgon	1 g
Sodium sulfite, anhydrous	40 g
Pyrogallol	6 g
Phenidone	2 g
Water to make	1 liter

Dilute one part of this solution with one part of water to make working solution. Development time is 10 min, 68°F (20°C), for Kodak Plus-X film or Agfa IF or ISS film, with exposure at the rated speed. The use of Developer D-512 should be restricted to high-contrast scenes and not be used for normal-contrast subjects.

DIVIDED DEVELOPMENT

Development in two solutions is an old processing technique. A multitude of variations exist. In some cases development is carried out in two separate solutions of the same developing composition. A given volume of D-76 developer has been found to provide more uniform development and less loss in emulsion speed during exhaustion when divided into two baths than when used as a single bath.[59] In other cases development may be started in a weak developing solution and finished in another of different activity.[60] But the most common form of divided development consists of a first solution that contains the developing agents and sodium sulfite without alkali present. No image is developed in this solution. When the photographic material is transferred to an alkaline solution that is the second bath, the image is formed by the imbibed developing agents retained in the emulsion layer. In 1885 E. Audra[61–63] proposed such a two-bath developer and was one of the first to make use of the ability of gelatin layers to absorb a considerable quantity of processing solution. Audra's formula for the first developing solution was as follows:

Sodium sulfite	25 parts
Distilled water	100 parts
Sulfuric acid	1 drop/30 ml
Pyrogallol	10 parts

For use, one part of this solution was combined with ten parts of water. The photographic plate was immersed for more than a minute, drained for 3 or 4 sec, then immersed in

Sodium sulfite, 25% solution	10 parts
Sodium carbonate, saturated solution	3 parts
Water	100 parts

The developing agent—pyrogallol—was imbibed in the gelatin layer of the photographic plate in the first solution, then activated in the alkaline second solution. This processing technique evoked considerable interest and was quickly modified to suit the needs of others.[64–66]

The two-bath development procedure provides a fixed degree of development. A limited volume of solution containing the developing agent is absorbed in the emulsion layer in the first bath; only this given quantity is available to develop the image in the second solution. Two-bath development can produce results similar to compensating development, less image being formed in the highly exposed areas because of exhaustion of the developing agent. Such a condition may produce image-enhancing edge effects and possibly increased granularity. Development times and temperature are not critical, but the two solutions should be kept near the same temperature. A moderate degree of agitation may be necessary to both solutions to insure image uniformity. Overdevelopment is impossible when dilute solutions are used. Two-bath development has been suggested for overexposed film or for exposures of contrasty subjects.[67]

Scientific studies of two-bath development are scarce, but this technique was considered for motion picture film processing by J. I. Crabtree, H. Parker, Jr., and H. D. Russell.[59] They concluded that "In no case is it possible to obtain absolutely uniform development properties throughout the life of a developer, but by the use of two-bath developers this condition is approached much more nearly than with single-bath developers which are suitably revived. The two-bath developers give a practically constant gamma or degree of image contrast throughout their life, and the emulsion speed loss is less than with single-bath developers." In a single-bath developer, bromide ions accumulate, delaying the start of development. During this induction period it has been suggested[68–69] that the solvent effect of the sodium sulfite present causes a loss in latent image, reducing the film speed. In a two-bath developer, development should not occur in the first bath, so that no bromide ions are released. The time of immersion in the first solution should not be extended if sodium sulfite is present. Crabtree, Parker, and Russell added sugar to delay image appearance as well as sodium bisulfite to lower the

alkalinity of the first bath. They proposed a two-bath developer that required a 4-min immersion in each of these solutions for panchromatic films:

Formula SD-4

Solution A—First Bath	
Metol	5.0 g
Hydroquinone	2.0 g
Sodium sulfite, desiccated	100.0 g
Sugar	100.0 g
Sodium bisulfite	5.0 g
Water to make	1.0 liter

Solution B—Second Bath	
Sodium carbonate, desiccated	10.0 g
Sodium sulfite, desiccated	100.0 g
Potassium bromide	0.5 g
Potassium iodide	0.01 g
Water to make	1.0 liter

A more rapid-acting version of SD-4 was formulated by H. Parker and J. I. Crabtree.[70] Rapid Two-Bath Developer SD-6 was "satisfactory since it prevents excessive swelling, provides rapid and thorough hardening of the gelatin while in the developer, and allows the use of comparatively high processing temperatures. Also, it automatically eliminates the danger of overdevelopment and provides an almost constant degree of development in spite of variations in the time of treatment which can otherwise easily occur in hand processing for such short times." The time of treatment was 1 min in each bath without intermediate rinsing at a preferred temperature of 75 to 80°F. A water rinse or acid stop bath followed by fixation and a brief wash completed the processing. The formula for SD-6 two-bath developer contained:

Solution A	
Water (about 125°F [52°C])	500 ml
Metol	3 g
Sodium sulfite, desiccated	25 g
Hydroquinone	6 g
Sodium sulfate, desiccated	100 g
Sodium carbonate, desiccated	20 g
Water to make	1 liter

Solution B (two parts)

Part 1	
Water (about 125°F [52°C])	500 ml
Phenosafranine (1:1000 solution)	20 ml
Sodium sulfite, desiccated	50 g
Potassium bromide	2 g
Water to make	1 liter
Part 2	
Formalin (40% solution)	200 ml
Water to make	1 liter

To make solution B add equal volumes of part 1 and part 2 before using.

The popularity of the 35mm camera during the late 1930s and the 1940s caused continued interest in the two-bath processing of 35mm negatives to produce fine-grain and high-definition images. One of the early two-bath developers was proposed by E. Leitz and became subject to many variations. This developer consisted of:

	1938 Version[71]	Modern Version[72]
Solution A		
Water	1 liter	1 liter
Metol	3 g	5 g
Sodium sulfite, anhydrous	30 g	100 g
Solution B		
Water	1 liter	1 liter
Sodium carbonate, anhydrous	14.8 g	15 g
Sodium sulfite, anhydrous	3.24 g	6 g

Medium-speed film was immersed for 6 to 8 min in solution A, and 3 to 4 min in solution B, without a rinse between solutions. Solution temperature was 65°F for both solutions. Treat thin-emulsion film for 4 min in the first solution; for fast films the time of immersion is 8 to 10 min. Best results were said to be obtained when the normal speed of the film was multiplied by two.

The Leitz two-bath formula and several others were included in a summary of two-bath development by the magazine, *Miniature Camera World.* Table 5, a chart of two-bath formulas and processing directions, is derived from that magazine.[73]

Table 5. Summary of Two-Bath Development[a]

Ingredients	Leitz Two-Bath	Symon[74] (Modified DK-20)	Stoeckler High-Speed	Stoeckler Fine Grain	Agfa High-Speed	Jacobson (Formula 124)[75]	Meritol Caustic[76–80]	MCW 3[81,82]
Solution A								
Metol	5	5	2	5	5	5		2
Sodium sulfite (anhydrous)	100	100	100	100	30	100	90	60
Hydroquinone			5		10	2		7
Meritol							16	
Pot. thiocyanate		1.0						
Pot. bromide		0.5						
Cane sugar						100		
Sodium bisulfite						5		
Kodalk								6
Borax			2					
Water to (in liters)	1	1	1	1	1	1	1	1
Solution B								
Caustic soda (sod. hydroxide)			10[b]				100[b]	70[b]
Pot. bromide			10[b]					
Sod. carbonate (anhydrous)	15				125	10		(100[b])
Kodalk		20						
Borax				10				
Sod. sulfite (anhydrous)	6					100		
Water to (in liters)	1	1	1	1	1	1	1	1

[a] All weights in grams.
[b] Can be compounded from 10% stock solution.

Using the Two-Bath Table[73]

General: No preliminary wetting or forebath should be given, except in the case of Meritol-caustic which sometimes needs a one-minute soak with agitation in a one per cent (anhydrous) sodium sulphite solution to remove the film's coloured backing. The A bath should be poured into the loaded tank quickly and the film agitated for the times indicated (the shorter time being for the slower film) then poured out and re-stored. No rinse should be given, but B should be poured in and the film agitated for the times shown after which the B bath should be quickly poured out and an acid-stop used prior to the usual method of fixing. The B bath may in some cases be stored for further use, but it is so cheap that this seems scarcely worth while if consistent results are aimed at.

Leitz (Leica) two-bath: 3–6 min in A: 3 min in B, at a temperature of 65°F.

Symon: 6–15 minutes in A; the working B bath is made by diluting the stock bath to one-tenth its strength (to give a 0.2% solution of Kodalk) discarding it after use. Immerse the film for $3\frac{1}{2}$ min. in the B bath.

Stoeckler high-speed: Medium speed films need approximately $1\frac{1}{2}$ min. in A followed immediately by 30 sec. in B. Then use an acid stop bath immediately. (65°F.)

Stoeckler fine-grain: As for the Leitz two-bath.

Agfa high-speed: One minute with agitation at 70°F. in A followed by one minute with agitation in B and an acid stop bath. 5°F. rise or fall in temperature corresponds with about 25% decrease or increase in these times. Increasing the time in the B bath increases the contrast.

Jacobson (formula 124 from *Developing*): Films need about 5 min in A and about 4 to 6 min in B solution.

Meritol Caustic: Three minutes in each bath. The A bath must be diluted to a specified degree for each type of film.

MCW 3: Working at 65°F. (a) using the carbonate as the B bath give three minutes in each bath. The B bath is made by diluting the 10% stock solution "one in four"; (b) using the caustic solution as the B bath give one minute in A and two minutes in the B bath. The working bath is of 0.7% strength (this does not appear to be critical) and is made by diluting the stock bath "one in ten," throwing this away after use.

Two-Bath Development with Borax

The fine-grain development given by Kodak developer D-76 containing borax has spurred interest in the use of borax as the alkali in the second bath of a two-bath developer. Indeed, D-76 itself has been divided into two baths by Robert J. Starks. According to Paul Farber,[83] "The maximum emulsion speed afforded by D-76 is retained, along with the high acutance. However, the divided development gives the negatives a beautiful range of tones which straight D-76 cannot seem to do over a large range of contrast situations."

The formula for divided D-76 consists of:

Solution A

Metol	2.0 g
Sodium sulfite, desiccated	100.0 g
Hydroquinone	5.0 g
Potassium bromide	1.0 g
Water to make	1.0 liter

Solution B

Borax	50.0 g
Water to make	1.0 liter

Immerse film in solution A for 3 min, then in solution B for 3 min. Agitate the film for the first 5 sec of each minute. Another variation consists of developing the film for one-half the normal time in regular D-76, then transferring it for 2 min to a solution containing 5 g of borax and 30 g of sodium sulfite (anhydrous) in a liter of water.[84]

Metol is often stated to be the only developing agent which yields fine-grain images of good tonal gradation, as recently reiterated by L. B. Dalzell,[85–86] who proposed to improve the classic 1938 two-bath formula of Henrich Stoeckler by reducing the content of sodium sulfite to yield improved acutance. These solutions had the composition:

Solution 1

	Stoeckler (1938)	Dalzell (1967)
Water (40 to 50°C)	750 ml	750 ml
Metol	5 g	5 g
Sodium sulfite, anhydrous	100 g	75 g
Water to make	1 liter	1 liter

Solution 2

Borax	10 g	10 g
Water to make	1 liter	1 liter

Immerse film for 3 or 4 min in each of the two solutions, agitating every 30 sec in each. Uniform results were reported with 35mm Agfa ISS, Kodak Panatomic-X film (at index of ASA 100), Plus-X (ASA 160), and Tri-X film (ASA 400). The Stoeckler-made formula cited earlier in this section (1938 Leitz two-bath) contained only 30 g of sodium sulfite in the first solution.

Two-bath development, writes Helmut Gerlatzek,[87] "achieves a quality of detail in the shadows such as is unattainable in any other way while at the same time precluding all possibility of excessive density in the highlights." Gerlatzek, however, disagrees that Metol is the only developing agent that can provide fine-grain images with soft gradation. He proposed a Phenidone-hydroquinone first solution with low sulfite content:

Solution A

Water	1 liter
Sodium sulfite, anhydrous	50 g
Hydroquinone	5 g
Phenidone	0.3 g
Potassium bromide	0.5 g

Solution B

Water	1 liter
Borax, crystal	20 g
Boric acid	10 g
Potassium bromide	0.5 g

The film is first treated in solution A for 4 min with the usual agitation, the solution temperature being between 16 and 24°C. The film is drained briefly and then transferred without rinsing to solution B at 20°C for 4 min. The film is then briefly immersed in 2% acetic acid, rinsed in water, and fixed in the usual manner.

A Metol-hydroquinone first solution was proposed as early as 1938 by C. H. Shipman[88–90] with the option of a second bath of sodium carbonate or borax. The borax second solution was for the finer-grained images needed by small negatives. The formulations are given at the top of the next page. For use, temperature of solutions may vary from 70 to 80°F. Photographic material is immersed in solution A for 1 min, then drained but not rinsed before being placed for 1 min in solution B or 3 min in solution C. A similar divided developer has been recommended for tropical use.[91]

Solution A

Water (120°F for mixing)	946 ml
Metol	6.2 g
Sodium sulfite, anhydrous	32.4 g
Hydroquinone	6.2 g
Potassium bromide	2.6 g
Sodium chloride	0.2 g

Solution B

Water (120°F for mixing)	946 ml
Sodium carbonate, anhydrous	97.2 g

Solution C

Water (120°F for mixing)	946 ml
Borax	51.8 g

Paul Farber,[92] who has been active in promoting modern two-bath development, has proposed a Metol-hydroquinone solution of great versatility. The baths for Farber's divided developer consist of:

Solution A

Distilled water (80°F)	750 ml
Metol	6 g
Sodium sulfite, anhydrous	50 g
Hydroquinone	3 g
Potassium bromide	3 g
Sodium chloride (table salt)	0.5 g
Distilled water to make	1 liter

Solution B

Distilled water (80°F)	750 ml
Sodium sulfite, anhydrous	10 g
Sodium carbonate, monohydrated	50 g
Distilled water to make	1 liter

Solution C (Fine Grain)

Distilled water (80°F)	750 ml
Sodium sulfite, anhydrous	10 g
Borax (photo grade)	50 g
Distilled water to make	1 liter

Film is to be treated 2 min in solution A, then without rinse or stop bath, 2 min in solution B. Agitation is 5 sec every 30 sec in both baths. When using solution C, increase the immersion time to 4 min in this bath. Chemical modifications were proposed to change the performance of the divided developer. Increasing the sodium sulfite from 50 to 100 g in solution A will produce finer grain but will lower the edge sharpness between adjacent image details. Image contrast may be changed by varying the content of hydroquinone in solution A. Higher contrast can be obtained by increasing the hydroquinone concentration from 3 to 6 g (even higher with 10 g). Lower contrast resulted when the hydroquinone was present at a 1-g quantity or eliminated entirely. These modifications can also be employed when using solutions A and B as a two-solution paper developer. A 45-sec treatment in both baths, with an intermediate drain, was recommended with agitation in both baths.

Sodium metaborate can be formed by mixing borax and sodium hydroxide to produce a substance of higher alkalinity than borax. This invention of Harold D. Russell[93] has been sold in a hydrated form as Kodalk balanced alkali ($Na_2B_2O_4 \cdot 8H_2O$). Sodium metaborate, or Kodalk, has been used for preparing the second solution of a two-bath developer. For controlling the contrast of negatives exposed with harsh lighting, Ansel Adams[94] has proposed this two-solution developer:

Solution I

Metol	7.5 g
Sodium sulfite, desiccated	100 g
Water to make	1 liter

Solution II

Sodium metaborate (Kodalk)	10 g
Water to make	1 liter

Normal processing was 7 min in solution I, followed by a 3-min treatment in solution II. Continuous agitation is required in both solutions. Times in the first solution may be reduced depending on the desired image characteristics.

Pyrogallol is an active developing agent but is unstable in alkaline solution. Pyrogallol has been combined with Metol in the first solution of a two-bath developer that uses sodium metaborate in the second solution. The formulation, attributed to Larry Payne,[95] had the composition:

Solution A

Water (95°F)	800 ml
Sodium hexametaphosphate	2 g
Metol	2 g
Pyrogallol	3 g
Sodium sulfite	75 g
Potassium bromide	1 g
Water to make	1 liter

Solution B

Water (95°F)	800 ml
Sodium hexametaphosphate	2 g
Sodium metaborate	10 g
Sodium bisulfite	5 g
Water to make	1 liter

Development times are $2\frac{1}{2}$ min at 65 to 80°F in each solution. Agitation must be slow, gentle, and constant. This formulation is said to increase contrast with improved edge sharpness, and it should be useful for negatives exposed under flat lighting conditions. (See Figure 8.)

Two-Bath Developers for Photographic Paper

The processing technique of using two developing solutions for modifying the contrast of a photographic film or paper is well known. A recently patented two-step method for film development used a relatively high Phenidone content in the first PQ developer and a much lower Phenidone content in the second PQ developer.[96] Such a practice is designed for contrast control rather than achieving high-definition images. Usually, one

paper developer is primarily soft-working; the other is primarily a hydroquinone developer to produce contrast in the image. Mixing the two developers makes intermediate contrasts possible, although the extent of the contrast modification is limited. Image formation, for example, may be started in the soft-working developer; and finished in the other. Agfa 120 developer may be used as the soft-working solution and Agfa 130 as the solution to produce more contrast in the print.[97] The Kodak D-64 two-solution developer and the variable-contrast developer of Raymond F. Beers are also examples of such developers.[98] Ansel Adams states, "To me, this [Beers' two-solution formula] is one of the most useful of all formulas in that a wide range of contrast control is possible."[99] Adams has used sodium carbonate to replace the original potassium carbonate and he recommended varying the potassium bromide content to achieve the effect desired with each specific paper. For reference purposes, Adams' version of Beers' two-solution formula and mixing directions are given here.

Adams' Version of Beers' Formula

Solution A	
Water	750.0 ml
Metol (Elon)	8.0 g
Sodium sulfite, desiccated	23.0 g
Sodium carbonate, desiccated or monohydrated	20.0 g 23.4 g
Potassium bromide, 10% solution	11.0 ml
Water to make	1000.0 ml

Solution B	
Water	750.0 ml
Hydroquinone	8.0 g
Sodium sulfite, desiccated	23.0 g
Sodium carbonate, desiccated or monohydrated	27.0 g 31.5 g
Potassium bromide, 10% solution	22.0 ml
Water to make	1000.0 ml

Figure 8. Edge effects and compensating development are often produced by high-definition developers. Photograph (*a*) was made from a Kodak Royal Pan film negative processed in a Metol–sodium sulfite developer. Photograph (*b*) was made from a similar film negative processed without agitation in a thickened pyrogallol-sulfite developer. Ten times increase in exposure was needed for the last negative. Note the greatly improved tone rendition in the shadow area of the lower shelf as well as better line detail throughout photograph (*b*). (James King, Eastman Kodak Company)

The stock solutions are mixed in the following proportions to give a progressive range of contrasts. The lower-numbered solutions can be further diluted for very soft effects.

Contrast:	Low			Normal			High
Solution No.:	1	2	3	4	5	6	7
A	8	7	6	5	4	3	2
B	0	1	2	3	4	5	14
Water	8	8	8	8	8	8	0
Total	16	16	16	16	16	16	16

Figure 8. (*continued*)

Unlike this two-developer technique, divided development may be started in a sulfite-containing solution of the developing agents where little or no image is formed, then completed by immersing the print in an alkaline second bath. This two-bath development of prints was advocated in the early 1930s by Felix Formstecher.[100] A modern version has been proposed by Paul Farber[101] for the making of mural-sized photographic prints. The formulas for the two solutions consisted of:

Solution A

Metol	3.5 g
Sodium sulfite, anhydrous	40.0 g
Hydroquinone	10.0 g
Potassium bromide	3.5 g
Water to make	1.0 liter

Solution B

Sodium carbonate, monohydrate	100.0 g
Sodium sulfite, anhydrous	10.0 g
Water to make	1.0 liter

The photomural was swabbed on the emulsion side with solution A, making sure the entire surface was saturated evenly by the wetted sponge. This could take as much as 5 min and no image would appear. After the excess solution A was drained, another sponge was used to apply solution B. The image appeared almost instantly, and swabbing was continued for a few minutes until the image was formed completely. The print was then swabbed for 5 min with a rapid fixing bath, then spray-washed with water after a hypo-elimination solution treatment.

Water-Bath Development

"If a plate or film is placed in a developer for a short period, say 30 seconds, the emulsion will absorb a certain quantity of developer, and if the plate is now placed quietly into a dish of water the development will proceed so long as any non-exhausted developer remains in the emulsion, approximately about two minutes." Thus, in 1932, August Knapp[102] described a method of water-bath development that was to be named after him. The water-bath treatment can be repeated as many times as desired. The water-bath-developed image exhibited greater development of the shadow detail and less development of the highlights than occurred during regular one-solution development. Knapp claimed, "It is possible by this method completely to develop every atom of 'light-struck' silver in a plate without fear of producing undesirable density in the highlights, a result which, it is believed, has always been regarded as 'impossible'." [Many would still say this claim is impossible.]

Knapp cautioned that developing solutions containing hydroquinone were unsuitable, as would be alkali-rich solutions, unless used at low temperatures. Metol-hydroquinone developers were used with success, as were Metol-pyrogallol solutions.[103] He suggested a developing solution containing 0.7 g anhydrous sodium sulfite and 0.13 g Amidol in 29.6 ml of water. A three-cycle process would consist of soaking the photographic film for 40, 50, and 90 sec in the developing solution with a 2-min, horizontal, water immersion after each time in the developer. Knapp concluded, "The system has been a revelation, if in no other respect than that of controlling halation, the tendency being, curiously enough, to overdevelop somewhat the highlights

themselves, but within their margins and at their junction with less exposed areas, and not vice versa. This may perhaps be explained as a tendency to transfer the non-exhausted developer contained in the shadow portion of the emulsion to the neighboring highlights, after exhaustion or osmosis of the developer contained in the latter areas."[104]

Slowing development by transferring the developing image to a water bath was known and practiced long before Knapp, but the Knapp process did not require inspection during the image-forming period. Panchromatic plates could be easily treated. Some increase in graininess may result on some photographic materials, according to the tests of H. A. Robinson.[105] John B. Ehrhardt[106] proposed that film exposed to contrasty lighted subjects be soaked from one-fifth to one-half the normal development time in a standard developer such as Agfa 47, 17, and diluted 103, Kodak DK-50, D-76, and diluted D-72, then soaked for twice the normal developing time of that developer in a water bath. The photographic film is transferred to a tray and care is taken to avoid agitation. The Knapp system of water development was found by P. C. Smethurst[107,108] to be "the most useful in cases of known underexposure of any system yet put forward." Henry W. Bennett[110] proposed using the water bath for bromide paper printing from negatives of strong contrast.

Another form of restrained development, the invention of Frank Perry[111] and called the P. and H. Process, claimed improved detail definition. A twofold increase of speed was said to result. As described by H. C. Benedict,[112] "You merely immerse the film in a cold, concentrated developer for about a minute, squeegee the film, emulsion side down, to a plate of clean glass, and submerge the combination in water at normal room temperature for 15 minutes to several hours." The film is stripped from the glass, fixed, and washed. The recommended developer was Kodak DK-50 replenisher with potassium thiocyanate added. This solution, to be used undiluted, has the composition:

Water	1 liter
Metol	10 g
Sodium sulfite, desiccated	60 g
Hydroquinone	20 g
Kodalk	80 g
Potassium thiocyanate	4 to 8 g
Water to make	2 liters

Another modification of water-bath development involved using a second solution consisting of two parts of glycerin to five parts of water following

one-half normal development in Kodak DK-20 solution. This technique was proposed by Maximilian Heilbron,[113] who followed a 10-min development in DK-20 with two or three rinses in water and then a 15-min immersion in the glycerin solution to complete the image formation. An investigation of this technique by J. I. Crabtree and H. A. Miller[114] found that the slight acidity of the glycerol-water bath reduced the degree of development slightly as compared with a plain-water bath. The same result could be duplicated by reducing the normal developing time in the DK-20 by 35%. Emulsion contrast, speed, and graininess were the same for both the reduced-time DK-20 development and the two-solution DK-20-and-glycerol technique.

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Chapter 10
High-Energy Developers

The ubiquity of Metol hydroquinone, as a combined developer, is mainly due to its remarkable universality, which makes it possible to devise a single formula which can be used with equal success for plates, films, bromide and gaslight papers.

RICHARD B. WILLCOCK[83]

The phenylpyrazolidone-hydroquinone combination can give, under different conditions, any development solution necessary for the treatment of negative and positive materials used in professional photography, as well as in that of the amateur.

ALFRED WIEDERMANN[9]

Fine-grain or high-definition developers are often the most suitable for processing the smaller-sized black-and-white negatives, especially those of the 35mm size. Such developers may be used with larger-sized films as well. However, because of the greater film area, negatives of this size do not require the graininess and acutance characteristics so essential to the 35mm size. High-energy developers are often used for developing these larger-sized negatives. This type of developer is rapid acting (short development times)

and yields maximum latent image amplification (high film emulsion speed). Special high-energy developers may be compounded to yield extremely high image contrast, such as for commercial, industrial, or press photography, or for process work in the printing field.

HIGH-ENERGY DEVELOPERS

The high-energy developer consists of one or more developing agents in an alkaline solution that is considerably higher in pH than other kinds of developers. Hydroquinone can be activated by sodium or potassium hydroxide to yield very high contrast. But for rapid development yielding a full range of tones, especially good shadow detail, general-purpose developers of the high-energy type are usually formulated from two developing agents. The combination of Metol-hydroquinone (MQ) has proven to be highly successful in producing images of high emulsion speed with excellent tonal scale. The greatest number of general-purpose developers are MQ formulations, although in recent years some have been replaced by formulations of Phenidone-hydroquinone (PQ developers).

Metol and Phenidone are rapid-working developing agents that produce low-contrast images at moderate solution alkalinity. Neither of these developing agents is sensitive to the presence of bromide or iodide ions released by development, so they are capable of unrestrained action in film areas having only very slight exposure. Hydroquinone is quite different in action, being slow working at moderate alkalinity and yielding images of high contrast (little shadow detail). Hydroquinone is restrained by bromide or iodide ions and acts only poorly in areas of low exposure. By combining Metol or Phenidone with hydroquinone it is possible to formulate a developer that will be suitable for almost any purpose. Generally, for normal contrast, twice as many grams of hydroquinone are used as of Metol; for lower-contrast formulations, the amount of hydroquinone is often reduced; for higher-than-normal contrast, at least four times as many grams of hydroquinone as of Metol may be used, often with additional alkali (sodium or potassium carbonate). From about 0.5 to 2.0 g of potassium bromide per liter of solution are usually present as the restrainer in most MQ formulations.

Superadditivity

The combination of Metol or Phenidone with hydroquinone produces a development that is greater than the sum of the development given by separate developers containing the same quantity of each developing agent. This more-than-additive action was nicely illustrated by G. I. P. Levenson,[1] who used a hydroquinone developer to produce a density of 1.0 on a film. The

film was then washed in the dark to remove the developer from the gelatin layer. Because the film had already been developed to a density of 1.0, any further development would start immediately, without delay, as the induction period had already been passed. He then put this washed film into three developers: (1) a Metol developer, (2) a hydroquinone developer, and (3) a combined Metol-hydroquinone developer. This MQ developer contained the same concentrations of Metol and hydroquinone that were present in the other two developers. Each of the three solutions was at the same pH (about 10), the same temperature, and used with similar processing conditions. At the end of one minute, development was stopped and the growth in density was measured.

Developer	Density Growth in One Minute (from 1.0 original density)
1. Metol	0.3
2. Hydroquinone	0.1
3. Metol-hydroquinone	0.6

The combined rates of (1) Metol + (2) hydroquinone developers was 0.4 density units per minute but the rate of the (3) combined Metol-hydroquinone developer was 0.6 density units per minute, a 50% increase in rate for the MQ developer.

The superadditive developing action given by Metol-hydroquinone or Phenidone-hydroquinone developers has been studied extensively. As with all theoretical interpretations of practical events in photographic processing, there is still some question of the mechanism of the nature of superadditivity. Levenson[2] has proposed that Metol is the primary developing agent in an MQ developer, engaged in the electron transfer that produces the metallic silver of the image. At moderate alkalinities hydroquinone serves primarily to convert the oxidized Metol back to the original reduced form, thus regenerating and maintaining the concentration of the active Metol. More hydroquinone is oxidized in an MQ developer than Metol, the quinone being removed as the sulfonate by the action of the sodium sulfite of the developing solution.

A similar mechanism has been proposed by A. J. Axford and J. D. Kendall[3] for Phenidone-hydroquinone developers. They state that "In the Phenidone/hydroquinone system, therefore, it is suggested that development is initiated by the Phenidone component with the production of a free radical, which is immediately reconverted *in situ* to the pyrazolidone ion by the acceptance of an electron from the hydroquinone ion, which then sulphonates." These authors found that the maximum rate of development for an MQ series of developers was obtained when the molar percentage of Metol was 28%; the

maximum rate of working of PQ developers occurred when the Phenidone was at a molar percentage of 7%—that is, the molar ratio of Phenidone to hydroquinone was 7:93. It was concluded that Phenidone was about 18 times more efficient an activator than Metol in combination with hydroquinone in practical developers. Axford and Kendall[4] have also found that "alkyl substituents in either the 4- or 5-position do not differ materially from Phenidone itself in their ability to form superadditive combinations with hydroquinone." The maximum rate of development occurred when the percentage molar ratio of the substituted Phenidone to hydroquinone was about 7 to 10%.

Some representative formulas of MQ developers are given in Table 1. Slight modifications of basic formulas have produced a whole family of MQ developers suitable for almost any purpose. Increasing the proportion of hydroquinone to Metol or increasing the alkali content, or both, increases the contrast and density produced. Increased contrast may be obtained by using the undiluted stock solution or a lesser dilution of a developer that is normally diluted for use. Shortening the developing time or increasing the dilution softens the normal contrast. Thus, a developer such as DK-50, normally used without dilution, may be diluted with water to secure better control of contrast with improved acutance properties.

Role of Phenidone

One modern modification of standard MQ developer formulas has been to replace the Metol by Phenidone. The amount of Phenidone required is only about one-fifth to one-tenth the amount of Metol it replaces. PQ developers are not as sensitive as MQ developers to the restraining effect of the bromide and iodide that accumulates in the emulsion layer and the solution during processing. This type of developer is thus especially useful for continuous machine processing of negatives.[5] Because potassium bromide is relatively ineffective as a development restrainer of fog, organic restrainers, such as benzotriazole, are often present in PQ developers.

Phenidone has the added advantage that it does not cause dermatitis on the skin of those people who may have become sensitized to the presence of an impurity in the Metol in MQ developers. Ermen[6] reported this impurity to be a derivative of *p*-phenylenediamine

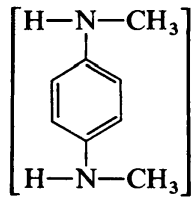

Table 1. General-Purpose MQ Developers

	Gevaert G-212	Gevaert G-214	Gevaert G-201	Kodak DK-50	Kodak D-61a	Kodak D-11	Ilford ID-2
Warm water (125°F [52°C])	750 ml	750 ml	750 ml	500 ml	500 ml	500 ml	750 ml
Metol[a]	2.0	2.0	1.5	2.5	3.0	1.0	2.0
Sodium sulfite (anhydrous)	25.0	25.0	50.0	30.0	90.0	75.0	75.0
Sodium bisulfite	—	—	—	—	2.0	—	—
Hydroquinone	1.5	3.0	6.0	2.5	6.0	9.0	8.0
Sodium carbonate monohydrate	35.0	19.0	35.0	—	14.0	30.0	43.0
Kodalk	—	—	—	10.0	—	—	—
Potassium bromide	0.5	1.0	2.0	0.5	2.0	5.0	2.0
Cold water to make	1.0 liter	1.0 liter	1.0 liter	1.0 liter	1.0 liter	1.0 liter	1.0 liter
Dilution for use (tank)	None	1:1	1:4	None	1:3	None	1:5
Processing time (minutes)	$4\frac{1}{2}$	4 to 8	6 to 8	5 to 10	12	5	6 to 12
Contrast	Low	Normal	Contrasty	Normal	Normal	Contrasty	Contrasty

[a] Unless indicated otherwise, all quantities are in grams.

The final oxidation product of Phenidone is colorless, so that a PQ developer has less tendency to stain than a comparable MQ developer. All of these advantages, coupled with the ability of Phenidone to produce high emulsion speed, has caused many MQ formulas to be converted to PQ formulations; unfortunately, these have usually been made available only as proprietary products. Some typical examples of published PQ developers for negative development are given in Table 2.

Alfred Wiedermann[9] has noted that "The superadditivity and the variations in alkalinization confer such a flexibility upon the Phenidone-hydroquinone developers that they can answer all photographic needs." PQ developers are versatile, indeed, and often one universal formula need only be diluted to suit many needs. Stock solution ID-62, for example, may be diluted 1:1 (development time: 45 to 60 sec, 68°F) for use with contact-speed photographic papers; at a dilution of 1:3 the working solution is recommended for the development ($1\frac{1}{2}$ to 2 min, 68°F) of photographic enlarging papers. For tray development of films and plates a 1:3 dilution of the ID-62

Table 2. Some PQ Developers for Negative Development

				Wiedermann[9]	
	ID-62[7]	ID-67[7]	Willcock[8]	RSC	TEA
Warm water (125°F [52°C])	750.0 ml	750.0 ml	750.0 ml	750.0 ml	750.0 ml
Sodium sulfite (anhydrous)[a]	50.0	75.0	100.0	125.0	125.0
Hydroquinone	12.0	8.0	30.0	16.0	20.0
Sodium carbonate (anhydrous)	60.0	37.5	—	60.0	—
Sodium hydroxide	—	—	25.0	—	—
Triethanolamine	—	—	—	—	80.0
Phenidone	0.5	0.25	1.5	1.0	1.2
Potassium bromide	2.0	2.0	3.5	9.0	7.0
Benzotriazole	0.2	0.15	1.0	3.0	—
Water to make	1.0 l	1.0 l	1.0 l	1.0 l	1.0 l
Dilution (tank)	1:7	1:5	1:30	1:50	1:20
Time of development (min)	4 to 8	5 to 10	7	12 to 20	10 to 13

[a] Unless indicated otherwise, all quantities are in grams.

stock solution requires from 2 to 4 min, 68°F; for tank use, the recommended dilution is 1:7 with a development of 4 to 8 min at 68°F.

HIGH-CONTRAST DEVELOPERS

The contrast of an MQ developer may be increased by using greater quantities of hydroquinone, the developing agent commonly used to produce higher densities and contrast. From about four to 10 times (sometimes more) as much hydroquinone as Metol may be used. The presence of the Metol helps speed the start of development, as hydroquinone alone has a considerable induction period before development begins. Metol, however, tends to promote development of the lesser-exposed silver halide crystals, causing lowered image contrast. Increased potassium bromide is often used to counteract this loss of contrast by MQ developers designed for high contrast. The bromide also helps to control the nonselective development given by energetic solutions often made alkaline with high concentrations of sodium carbonate. Minute concentrations of potassium iodide are often used with potassium bromide to control fog in contrast developing solutions. J. Southworth[10] used potassium bromide and potassium iodide for a developer that "may solve the problem of obtaining high contrast together with an adequate rendering of shadow detail in high-speed plates under conditions of minimum exposure." The formula for this solution contained:

Metol	2 g
Sodium sulfite, crystals	100 g
Hydroquinone	12 g
Sodium carbonate, crystals	75 g
Potassium bromide	4 g
Potassium iodide	0.02 g
Water to make	1 liter

Maximum contrast was said to be reached in 6 to 8 min, 18 to 21°C.

MQ developers activated by carbonate give contrasty image development suitable for certain commercial and industrial applications or for the development of aerial films. However, for very high contrast, such as for copying, photomechanical papers, X-ray, and process work, developers are often compounded with a high concentration of hydroquinone as the sole developing agent. Maximum activation of this developing agent requires the presence of sodium or potassium hydroxide, as the carbonates are inadequate alkalis for this purpose. Kodak developer D-8 is an example of the hydroquinone

Table 3. Contrast Developers

Ingredient[a]	Kodak D-19	Kodak D-72	Kodak D-8	Ilford ID-13	Ilford ID-72	Wiedermann Document	Wiedermann PQ X-Ray	Willcock No. 2
Water (125°F [52°C])	500 ml	500 ml	750 ml	750 ml	750 ml	750 ml	750 ml	750 ml
Metol	2.0	3.0	—	—	—	—	—	—
Sodium sulfite, desiccated	90.0	45.0	90.0	—	72.0	120	150	100
Potassium metabisulfite	—	—	—	12.5	—	—	—	—
Hydroquinone	8.0	12.0	45.0	12.5	8.8	26	20	30
Phenidone	—	—	—	—	0.22	1.0	1.0	1.5
Sodium carbonate, monohydrate	52.5	80.0	—	—	48.0	—	—	—
Potassium carbonate	—	—	—	—	—	110	75	—
Sodium hydroxide	—	—	37.5	—	—	—	—	25
Potassium hydroxide	—	—	—	25	—	—	—	—
Potassium bromide	5.0	2.0	30.0	12.5	4.0	15.0	8.0	3.5
Benzotriazole	—	—	—	—	0.1	1.0	0.5	1.0
Cold water to make	1.0 liter	1.0 liter	1.0 liter	1.0 liter	1.0 liter	1.0 liter	1.0 liter	1.0 liter
Dilution	None	None	2:1	None	None	1:2	1:2	None
Time (min at 20°C)	5	1 to 3	2	3 to 5	5	2 to 4	5	½ to 1

[a] All quantities are in grams unless indicated otherwise.

contrast developer of high alkalinity, containing 45 g of hydroquinone and 37.5 g of sodium hydroxide in a liter of developing solution. (See Table 3.)

High-contrast images have been obtained not only on process films and plates but also on high-speed negative films by J. Rzymkowski[11] through the use of a catechol developer. The light-sensitive photographic material was exposed through the base. Development was for 6 min, 23°C, in a solution containing 12 g catechol, 30 g sodium hydroxide, and 12 g potassium bromide in a liter of water. The gelatin is made less soluble (tanned) in the regions where development has occurred but is not changed in the undeveloped regions. During the development period the gelatin in the unexposed or very weakly exposed areas is dissolved in the strongly alkaline solution. A very high-contrast image remains. This technique is limited to those special photographic materials (with low gelatin hardening) that can be exposed through the base.

Quantities less than 2 g/liter of Phenidone may be combined with high concentrations of hydroquinone to provide developers of high contrast for document copying, X-ray, and other purposes. PQ concentrated developers were compounded by Wiedermann.[9] His formulations included 20 to 26 times as much hydroquinone as Phenidone in the presence of a considerable quantity of potassium carbonate. Both potassium bromide and benzotriazole were needed as restrainers. Willcock[8] achieved a 30- to 60-sec development time with the undiluted version of his developer that contained 30 g hydroquinone and 1.5 g Phenidone in a liter of solution with 25 g sodium hydroxide (See Willcock No. 2 in Table 3 for formula.)

Some typical compositions of contrast developers are given in Table 3.

DEVELOPMENT FOR MAXIMUM EMULSION SPEED

Many conditions in photography provide less exposure than the minimum required by the rated speed of the film emulsion. Dim lighting, the need to use small lens apertures to secure the desired depth of field, the necessity of high shutter speeds to stop fast action, the increased exposures required by extreme close-up photography, and the use of slow-speed telephoto lenses, or a combination of a number of these, often require a film of greater sensitivity than is provided by conventional processing of the available film products. Increasing the time of development, sometimes called "pushing" development, will give a slight increase in film emulsion speed of negative films but with the risk of enhanced contrast, increased grain size, and other detrimental image characteristics. One film manufacturer states "push-processing does not *significantly* increase the speed of the film."[12]

Securing maximum film speed may involve more than just the use of a suitable developer. The film emulsion may be treated before exposure (hypersensitizing), or after exposure but before development (latensification), or the processed silver image of the negative may be increased in density by an aftertreatment (intensification). Most of these methods are not used very much for modern photographic materials, but the use of such treatments tends to recur, so suitable methods will be discussed in this chapter and in Chapter 1 of Volume 2. Any one, or more than one, of these speed-enhancing treatments may be useful to secure an adequate photographic image under unfavorable photographic conditions, but it would be most convenient to gain maximum film sensitivity by the use of a high-speed film processed in a suitable developing solution. This would eliminate the need for additional film treatment either before or after development.

A developer formulated to produce maximum emulsion speed is essentially a developing solution for underexposed film. The developer must be capable of reducing the silver in crystals that have only weak latent images. It must be able to distinguish between these weakly exposed crystals and the crystals with no exposure. No practical developer has absolute differentiation between the exposed and the unexposed crystals; rather, it reduces those with latent image faster than those without it. The weakly exposed silver halide crystals, whose development is so necessary for maximum speed utilization, are reduced only slightly faster than the unexposed. Practical maximum-speed developers often give high fog because their restrainer content is very low in proportion to the chemical activation of the developing agents. The standard developer formulas supplied by photographic film manufacturers often possess more restraint, because low fog is highly prized by the film emulsion maker. Chemical supply houses that do not manufacture film often supply photographic developers with less restraint, yielding higher fog but giving more development of weakly exposed silver halide crystals—that is, higher emulsion speed.

Image formation must exceed fog formation, so the practical limitation on special speed-producing developers is that the development must be stopped when the maximum distinction exists between the weakly exposed and the unexposed regions. Generally, this is less than maximum development, which would yield maximum emulsion speed, but the high fog given by maximum development may reduce the distinction between the exposed and unexposed silver halide crystals. Long-term development—development to finality—may actually give less image differentiation than a shorter time of development and may produce undesirable high contrast. Any developer for maximum film speed involves the control of both fog and image contrast in order to be efficient in providing maximum image discrimination.

Are any of the developing agents, or combinations of developing agents,

more suitable than others for producing maximum film emulsion speed? This was the question considered by T. H. James[13] in his experiments with air-free developing agents (0.005 *M*), the solution also containing potassium hydroxide (0.04 *M*) and potassium bromide (0.0066 *M*). Except for a ferrous oxalate developer, all developing solutions had a pH of 12.7 to insure that the developing agents were largely or completely in the active or ionized form.

Sodium sulfite was found to promote fog and to reduce the emulsion speed of hydroquinone development. Probably the emulsion speed loss was due largely to the removal by the sulfite of the accelerating intermediate, the semiquinone, of the hydroquinone. The fog density produced by the various developing solutions at complete development (finality) in one to two hours was in the range of 0.7 to 1.2. Development was carried out to produce a fixed fog density of 0.3, a much more practical value than for complete development. Similar contrasts measured as gamma were obtained under these developing conditions.

Hydroquinone (8.8 g) was also used in a developing solution containing anhydrous sodium carbonate (48 g) and potassium bromide (0.4 g) in a liter of solution. Metol, Glycin, and catechol did not respond favorably when used in this carbonate formulation. Pyrogallol and Amidol could not be used in the hydroxide formulation because of high fogging tendencies. These two developing agents were not included in the tests made by James.

Table 4 shows the relative speed and the image contrast (gamma) given by the solutions containing each developing agent or agents and for the D-19 developer. When the speed was multiplied by the gamma, a number, called the "degree of perfection," was obtained for each agent. The higher this number, the more effective was the agent for use in maximum-speed developing solutions. The variation in speed and gamma for the first eight developers in the table is rather small. Metol or hydroquinone (caustic) were essentially equal in effect. The lowered gamma given by catechol was presumed to be due to the destruction of small latent image centers on neighboring crystals by the migration of the oxidation product of catechol. The presence of sodium sulfite would cause a substantial increase in gamma for equivalent development.

T. H. James summarized his results by concluding:

The close correlation between gamma and speed values for a number of developing agents of widely different chemical constitution indicates a sharply defined minimum exposure required for developability. The critical size and configuration of the latent-image center which will just promote development of a given grain must be substantially the same for each agent. On the other hand, development by hydroxylamine and *p*-aminophenylglycine apparently is not promoted by such centers. A heavier exposure is required before the grain becomes developable by these agents. This may also be true

Table 4. Development Carried to Fog Density of 0.3

Agent	Relative Speed	Gamma	Degree of Perfection
Diaminodurene	100.0	2.55	255
Hydroquinone (carbonate)	100.0	2.60	260
p-Amino-*o*-cresol	97.7	2.65	259
Catechol	97.7	2.30	234
p-Aminophenol	95.5	—	—
Ferrous oxalate	95.5	2.56	244
Metol	93.3	2.70	252
D-19 developer	93.3	2.56	239
Metol monosulfonic acid	91.2	2.54	232
Hydroquinone (caustic)	83.2	2.64	220
Hydroxylamine	77.6	1.68	131
p-Aminophenylglycine	74.1	1.81	134
p-Hydroxyphenylglycine	64.6	2.42	156
Ascorbic acid	40.8	2.58	105

for ascorbic acid and *p*-hydroxyphenylglycine. The fact that the speed, relative to the standard, is increasing right up to maximum development indicates that the growth of fog is complicating the situation.

The speed and gamma values obtained during the earlier stages of development may vary considerably according to the nature of the developing agent, and the disparity is often great. Thus, hydroquinone may give less than one-tenth the speed of diaminodurene or Elon when development is carried to equally low gamma values. The early stages of development are much more sensitive to kinetic factors which affect the rate of initiation of development in the individual grains, and which may vary with exposure to a far greater extent for one developer than for another.

The conclusions of James are of important theoretical interest, but practical developers must contain sodium sulfite for protection, as the developing solutions are used in air. The high contrasts may not be suitable for practical situations. Speaking of practical developing solutions, R. B. Willcock[14] has pointed out that "Developers of excessively low reduction potential such as glycin [Glycin] and hydroquinone will give still greater sensitivity depression and materially alter the curve shape in comparison with results obtained with surface-acting high reduction potential developers. By a careful choice of developer it is possible not only to vary the threshold sensitivity of an emulsion but to alter its characteristics."

Willcock notes that most developers of fairly high reduction potential will cause surface development and depress the formation of high densities in areas of great exposure. Metol, pyrogallol, and catechol are recommended for developers for increasing emulsion speed. MQ developers, when highly diluted, give surface development and limit the growth of density in areas of maximum exposure. Developer composition may influence the degree of increase of emulsion speed, but the inherent contrast of the photographic film and the contrast of the subject also influence the final results obtained. In poor light at small camera apertures, Willcock concludes, emulsion speed increases of more than two times are difficult to exceed.

Catechol Developers

As maximum emulsion speed developers, R. B. Willcock[15] proposed two Metol and one catechol developing solutions:

	Metol No. 1	Metol No. 2
Water (125°F [52°C])	750 ml	750 ml
Metol	10 g	16 g
Sodium sulfite (anhydrous)	60 g	150 g
Potassium metabisulfite	—	15 g
Sodium carbonate (anhydrous)	90 g	—
Sodium hydroxide	—	14 g
Potassium bromide	2 g	5 g
Water to make	1 liter	1 liter

At 1:1 dilution, development time at 68°F for a sheet film was 4 min for the No. 1 solution and $2\frac{1}{2}$ min for the No. 2, but for maximum emulsion speed, increases of 50 to 100% beyond these development times were suggested.

The catechol developer, said to give good threshold development, consisted of two solutions.

No. 1 Solution	
Catechol	20 g
Potassium metabisulfite	10 g
Water to make	500 ml

No. 2 Solution	
Sodium hydroxide	15 g
Water to make	500 ml

For use, take one part of the No. 1 solution, one part of the No. 2 solution, and 15 parts of water. At 68°F a development time of 12 min was used with a sheet film. Catechol has long had a reputation as a suitable developing agent for the treatment of underexposure. The use of very low or no sulfite with catechol will produce an image stain that enhances the image silver density, but the unprotected developing agent is oxidized rapidly. The developer loses energy quickly, limiting the production of high densities in the areas of greater exposure.

Pyrogallol Developers

Developing solutions containing pyrogallol with low or no sodium sulfite also produce a stain image that reinforces the silver image. Richard B. Willcock[16] mentions that such developers are capable of producing fine detail with rapid development of possibly underexposed photographic materials. The Photographic Section of the Royal Flying Corps used a staining pyro-Metol developer during the 1914–1918 war. In his book, John Erith[17] lists the RAF pyro-Metol staining formula as follows:

Part A

Metol	9.1 g
Potassium metabisulfite	10.4 g
Pyrogallol	10.4 g
Potassium bromide	3.9 g
Water to make	2366 ml

Part B

Sodium carbonate, crystals	255.2 g
Water to make	2366 ml

Use equal parts of part A and part B for staining development, discarding the solution after one-time use.

Low-sulfite pyrogallol or catechol developers produce an imagewise stain that helps improve shadow detail. The gelatin is also tanned imagewise; that is, the metallic silver image particles are encased in a toughened gelatin layer of low solubility. J. Rzymkowski[18] has reported "that tanning development tans the gelatin below the threshold value of the silver image." He proposed to expose the photographic material through the support, develop in a sulfite-free catechol (2 g/l) and potassium hydroxide (2%) solution, treat with

40°C water to remove untanned gelatin areas of the image, and then dye with 1% nigrosin, a black dye. Both contrast and threshold sensitivity were said to be increased considerably. Rzymkowski concluded that "Even compared with normal M.Q. developer the tanning developer gives an increase in sensitivity of at least three to four times. The method is not universally applicable since it requires specially prepared gelatin emulsions."

Meritol Caustic Developers

Meritol caustic development, according to Willcock's evaluation in 1954,[15] "is capable of giving higher emulsion speeds than any other methods published hitherto, certainly up to four times normal for average subjects, and even up to six times for subjects of medium brightness range." Meritol is a chemical combination of *p*-phenylenediamine and catechol. This combined developing agent is not currently recommended for modern film materials, although some enthusiasts find it worthy of use.[19–23] Meritol caustic is a two-bath formulation of the following composition:

Meritol Caustic Developer

Solution A	
Sodium sulfite (anhydrous)	90 g
Meritol	16 g
Water to make	1 liter

Solution B	
Sodium hydroxide (10%)	66 ml
Water to make	1 liter

A prebath of a minute or two in 1 to 2% sodium sulfite is sometimes given to remove the backing dyes from certain films whose dye is not discharged in the above solutions. The A bath must be diluted before use, depending on the type of film. Three minutes in diluted bath A followed by 3 min in bath B, with no rinse between baths, is the method of processing with Meritol caustic. An acid stop bath is recommended after the caustic bath before the film is put in the fixing bath. For most consistent results, fresh solutions should be used for each processing session. If Meritol cannot be obtained, 16 g of Meritol can be replaced by 7 g of para-phenylenediamine together with 9 g of catechol.

Immersion of a film in a caustic bath may soften the gelatin of the emulsion layer. Reticulation or frilling of the emulsion layer may degrade the image. R. B. Willcock[24] suggested adding 20 ml of formalin to each 500 ml of caustic solution. Meritol caustic two-bath treatment appears to have its greatest usefulness with high-contrast subjects. The exhaustion of the developing agents in the areas of high exposure will cause a depression of density in these areas but provides full threshold development. Other developing agents—Metol, MQ, catechol, or *p*-aminophenol—may also be used with a caustic afterbath. The first solution with the developing agents should not be active enough to form appreciable developed image during the time of film immersion. The greater the degree of this development, the higher the resulting image contrast. Much of the depression of the high image densities may be lost if appreciable development occurs, thus defeating the purpose of the two-bath treatment.

MAXIMUM-ENERGY DEVELOPERS

Staining and tanning developing solutions have a short solution life because of the low concentration of preservative. Kodak D-82 maximum-energy developer is a concentrated Metol-hydroquinone solution that contains considerable sulfite to preserve the caustic solution. This developer has been recommended for underexposures. The formula is as follows:

Kodak D-82 Maximum-Energy Developer

Water (about 125°F)	750 ml
Methyl alcohol	48 ml
Metol	14 g
Sodium sulfite, anhydrous	52.5 g
Hydroquinone	14 g
Sodium hydroxide	8.8 g
Potassium bromide	8.8 g
Cold water to make	1.0 liter

Develop from 4 to 5 min at 68°F or 20°C. This highly energetic solution may give fog or excessive contrast with some photographic materials.[25]

The quest for maximum speed in a photographic material usually involves accepting an image of lowered quality, using special development techniques, or using a developing solution of decreased stability. As G. I. P. Levenson[26] has stated,

The best conditions for coaxing the maximum emulsion speed from a given material can only be decided by trial-and-error experimentation. Each type of film or plate has to be treated separately, and checks need to be made on each batch of any particular type.

In general, and neglecting differences, full development in solutions such as **D.76** and **D.23** will reveal the highest emulsion speed of which the emulsion is ordinarily capable. In my experience, **D.76** has always equalled, and has sometimes surpassed, the sensational proprietary super-speed developers, not only for speed but for fineness of grain.

Hydrazine Developers

Hydrazine, $NH_2—NH_2$, was used as a developing agent as early as 1891 by Momme Andresen.[27] According to more recent work by T. H. James,[28] four atoms of silver are reduced for each molecule of hydrazine that is oxidized. Nitrogen gas is evolved during development. Reduction of the silver requires a pH of at least 12 with a strong tendency to fog the silver halide indiscriminately. G. I. P. Levenson[29] found that as the pH of a hydrazine developer was raised from 12.2 to 13.9, the shape of the developed silver particles changed from spheroidal to filamentary, apparently indicating a shift from physical development to a more direct chemical development.

Developers containing hydrazine as the sole developing agent have achieved little practical importance because of their indiscriminate reduction of silver at the high pH needed to activate the compound. In 1948 Adrian Peter Herman Trivelli and William Farrell Smith patented the addition of hydrazine to an MQ developer.[30] When hydrazine was used to bathe a sensitized film or the hydrazine was added to a developer containing normal photographic developing agents, significant increases in contrast and emulsion speed were achieved. Various hydrazines substituted on one nitrogen only or the hydrazides of various acids were effective but only when used with developing agents containing one or more phenolic groups, such as hydroquinone, catechol, *p*-aminophenol, or Metol. The speed-increasing effect of hydrazine developers is less with the highest-speed films.

Images produced in hydrazine-containing developers have increased contrast and speed but also have increased graininess of a type termed "woolliness." In addition, some photographic materials may exhibit a type of fog consisting of dots of high density ("pepper fog"). The increase in density given by the developer was attributed by R. Eliot Stauffer, W. F. Smith, and A. P. H. Trivelli[31] to the fogging of unexposed grains. Because this acceleration of development is not normally shown by either the hydrazine or the phenolic developers used alone, a product of the reaction of the hydrazine with the phenolic agent, or with an oxidation product produced during development, was thought to be formed. This reaction product could then diffuse to produce development of weakly exposed or unexposed silver

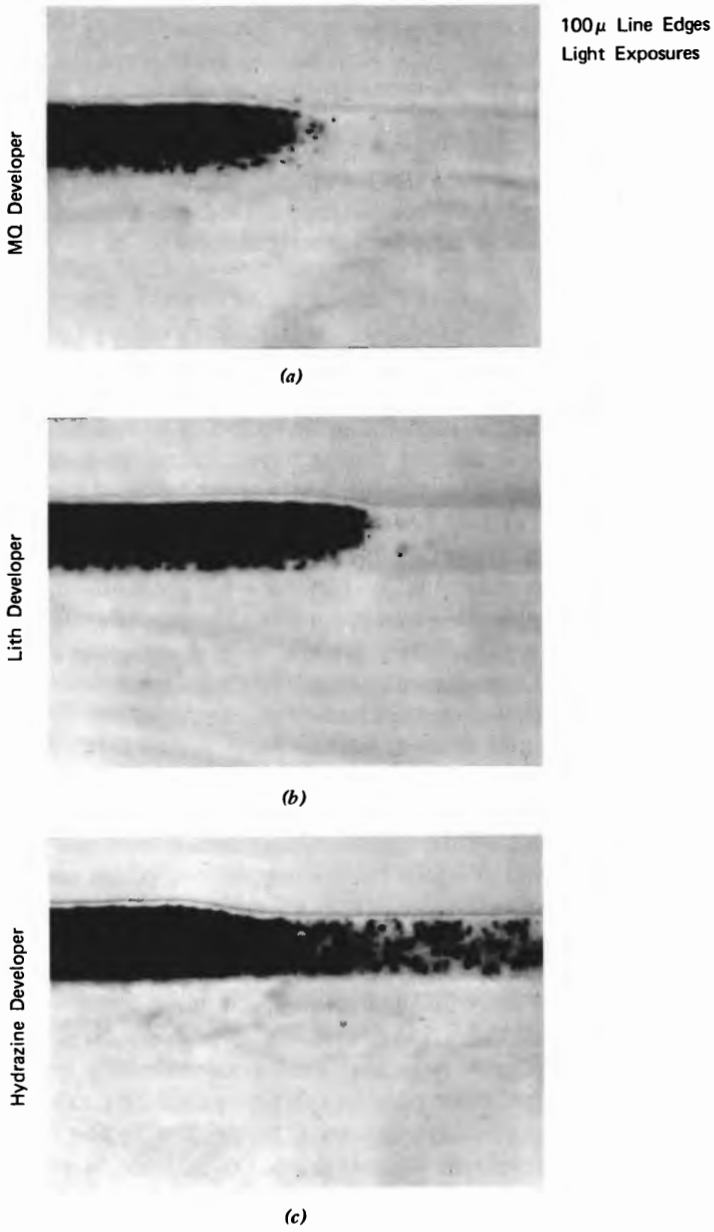

Figure 1. Photomicrographs at 1300× of the edge of a 100-μ line show the appearance of the edge after development of the film in (*a*) Metol-hydroquinone, (*b*) hydroquinone–low sulfite (lith), and (*c*) hydroquinone–hydrazine dihydrochloride developers. Note that the edge of the line has been obscured by the development of unexposed silver halide by the developer containing hydrazine. (Grant Haist and James King, Eastman Kodak Company)

halide crystals in the vicinity of exposed crystals undergoing normal development. Increasing the sulfite in the developer decreases the effectiveness of the hydrazine-containing solution, apparently by removing the speed-producing intermediate. (See Figure 1.)

This speed-increasing effect of hydrazine has been used by adding this compound to conventional developers, such as Kodak D-19 and D-72. Kodak SD-19a High Emulsion Speed Developer is the D-19 developer formulation to which a hydrazine compound and an antifoggant are added. According to H. A. Miller, R. W. Henn, and J. I. Crabtree,[32] who studied SD-19a,

> On the average, with high-speed negative films, development in Kodak SD-19a produces effective speeds more than double those obtained in conventional development.
>
> At ordinary fog levels, the emulsion speed given by Kodak SD-19a is not greater than in normal developers. As the time of development is increased, however, the fog density and the emulsion speed rise rapidly and the optimum speed is usually reached at fog levels around 0.40 above base. At higher fogs, the apparent graininess increases still more while the emulsion speed drops. However, fog levels varying considerably from the average optimum value of 0.40 give acceptable results, and the greatly improved emulsion speed may be expected over the fog density range from 0.25 to more than 0.75.

The quantity of hydrazine needed depends on the sulfite level of the developing solution to which the hydrazine is to be added. The antifoggant, 6-nitrobenzimidazole nitrate, produced increased image contrast in the underexposed regions, thus improving the emulsion speed. However, quantities of antifoggant above the optimum of 0.04 g/liter of SD-19a may result in considerable loss of emulsion speed. The exact optimum value of the antifoggant may have to be determined for the film material to be processed. The antifoggant is usually present in the same solution as the hydrazine before this solution is added to the developer, as is shown for SD-19a. The addition of hydrazine to developers having a pH below 10, such as D-23 or D-76, had little or no effect on the emulsion speed produced.

Kodak SD-19a High Emulsion Speed Developer

Solution A	
6-Nitrobenzimidazole nitrate, 0.2% solution*	20.0 cc
Hydrazine dihydrochloride	1.6 g
Water to make	30.0 cc

Solution B (Kodak D-19)

Water (about 125°F)	500.0 cc
Elon	2.2 g
Sodium sulfite, desiccated	96.0 g
Hydroquinone	8.8 g
Sodium carbonate, desiccated	48.0 g
Potassium bromide	5.0 g
Cold water to make	1.0 liter

* To prepare a 0.2% solution of 6-nitrobenzimidazole nitrate, dissolve 2 g of the compound in one liter of distilled water (hot). 6-Nitrobenzimidazole nitrate is also available as Kodak Anti-Fog No. 2.

Dissolve chemicals in the order listed. To prepare a working solution, add 30 ml of solution A to one liter of solution B (developer D-19). Prepare the working solution just before use. No special equipment or processing techniques are needed for the use of developer SD-19a after the working solution has been prepared.

The best speed increase is obtained by developing for the time required to give a fog value around 0.40; although fogs up to 0.60 can be tolerated, they increase the printing time required for such negatives. The developing time will depend upon the temperature, processing equipment, and agitation. In general, with intermittent agitation in tray or tank, the correct time of development at 68°F with conventional high-speed negative materials is between 12 and 20 min. The optimum time can be determined for a particular emulsion by cutting a trial underexposure into three or more pieces and developing the pieces for a series of times ranging from 10 to 20 min. By this means the time of development can be selected which yields the lowest fog density at which a satisfactory increase in speed is obtained.

The speed-enhancing ability of SD-19a developer has been verified by many investigators. G. S. Moore[33] reported that this developer gave at least two to three times the speed over full development of the D-19 itself, which is a high-energy developer. Another research worker, P. Hariharan,[34] as have other users of developer solutions containing hydrazine, noted that solutions of SD-19a are unstable. Maximum speed with maximum fog is produced immediately after the solution is mixed and both quantities decrease with time. Most of the change occurs in the first 15 min after mixing. Granular fog ("pepper") may be produced when the solution is used with

minimum delay after mixing. After the initial change in activity, there is little variation in the characteristics of the developer for the next 24 hr.

As Hariharan[35] has concluded, "SD-19a developer, as a method of increasing film speeds, offers advantages only when an extremely low standard of definition can be tolerated. A substantial gain in speed, at very low levels of resolution, can then be obtained by initiating development with as little delay as possible after the working solution is mixed." The unstable characteristics of SD-19a developer and its degradation of the resolution and grain characteristics of the image make this developer of practical use only when an image cannot be obtained in any other way and must be obtained at any cost, such as has been the case with aerial reconnaissance during wartime.

DEVELOPERS FOR HIGH SPEED WITH LOW GAMMA

Many developers that produce high emulsion speed also yield images of high contrast. A developer for high speed with low gamma has been compounded by S. G. Bogdanov.[36] Bogdanov's developer, IIB-4, is essentially a modified D-19 formulation having, unlike D-19, extremely low concentrations of Metol and hydroquinone. By using a low concentration of developing agents with high reduction potential, Bogdanov was able to develop silver bromide crystals with less active latent image centers than are required for the D-76 developer.

The Bogdanov IIB-4 developer has the following formula (pH = 12):

Metol	0.25 g
Hydroquinone	0.25 g
Sodium sulfite (anhydrous)	25.0 g
Sodium hydroxide	0.66 g
Potassium bromide	6.0 g
Water to make	1.0 liter

This developer produced a speed increase of from one-half to one stop over D-76 developer at the same image contrast. The subjective image quality was slightly poorer than that given by the D-76 development. The developer solution has been reported to be relatively unstable, so that the speed gains were found to vary with the age of the solution.

It was unexpected that processing of film with low-activity, soft-working developers should produce images of better resolution and detectivity than

those produced by very active contrast-producing developers. Yet, the low-contrast, low-density images have been found to have less flare, lower granularity, improved resolution, and increased detectivity at constant exposure when the film is exposed to scenes of extended brightness range. Much investigative work of low-contrast processing has been carried out under U. S. governmental contracts.[37–38] Some of this research has been reported by A. Shepp and W. Kammerer.[39] Kodak Plus-X film was given a wide latitude exposure covering a range of 1:1,000,000, then developed for 4 min, 68°F, in Developer D-76 (1:1), Developer D-19, or in low-contrast developer T/O XDR-4.

Developer T/O XDR-4

Potassium sulfite	25 g
Metol	1 g
Hydroquinone	1 g
Potassium bicarbonate	10 g
Water to make	1 liter

The moderate low-density, low-contrast image produced by development in the T/O XDR-4 solution showed retention of fine detail over the entire range of the exposure with suppressed flare. The active, high-contrast development produced increased flare, unprintable densities in the high exposures, and increased granularity. Shepp and Kammerer concluded that "The observed increased detectivity in overexposed images processed in low gamma developers is explained in terms of increased detectivity due to lower granularity."

Greatly increased film speeds, while maintaining fog and contrast at low levels, has been claimed for a developing solution patented by Arthur Zacchia.[40] Phenidone and hydroquinone are present in equal weight quantities at pH 11 in a solution designed for machine-processing of aerial films. Such a developer had the following composition (pH = 11.0):

Quadrafos*	2.0 g
Phenidone	1.8 g
Hydroquinone	1.8 g
Sodium sulfite	75.0 g
Sodium metaborate	75.0 g
Potassium bromide	3.0 g
Water to make	1.0 liter

* Available from Rumford Chemical Works, Rumford, R.I.

Two-rack development at 20 ft/min on a Kodak Versamat 11C-M processor corresponded to a development time of 26 sec at 85°F. A wide range of film contrast could be obtained on various aerial and Aerographic films by varying processing time without any serious loss in film speed.

Many exterior scenes have luminance scales that exceed 1000; that is, the brightness of the highlight is 1000 times that of the shadow area. Direct photography of the sun would exceed this value. Conventionally processed negatives are unable to record both shadow and highlight detail of scenes having very high luminance scales. Marilyn Levy[41] devised a Phenidone developer that would permit the recording of a very wide latitude exposure, such as a luminance scale of 1,000,000, while maintaining the maximum resolving power of the film.

The Levy developer, called POTA, consists of 1.5 g of 1-phenyl-3-pyrazolidone and 30 g of sodium sulfite in a liter of water. General-purpose negative films, such as Kodak Tri-X pan, Plus-X pan or Panatomic-X, when processed in POTA for 7 min yielded very low contrasts (gamma). Such a low-contrast negative made possible the recording of subjects with tremendous ranges of brightness, even the direct photography of the filaments of an electric light bulb.

The gamma of high-contrast films of very fine grain, such as Recordak Micro-File or Kodak High Constrast Copy film, may be reduced without speed loss in the POTA developer. A 5-min development of Recordak Micro-File, Type 5454, yielded slightly higher-than-normal image contrast with the emulsion speed improved over a 2-min, lower-contrast development of this film. Unlike the D-19 development of this film, where resolving power is critically related to optimum exposure, development in POTA produced a wide range of exposure where maximum resolving power was maintained. Indeed, resolving power increased at the highest exposures, a most unusual response for which Levy could offer no explanation. However, the POTA formulation has proven to be extremely valuable. For example, John Lutnes and Daniel Davidson[42] used POTA for processing astronomical plates. They reported that "IIa-D plates exposed on an astrosensitometer, developed in POTA, show retention of density information over an extreme brightness range and no change in minimum detectable intensity when compared with plates developed in D-76 and D-19."

Kodak High Contrast Copy film is an extremely fine-grained film even when developed to its normal high contrast. As Marilyn Levy first demonstrated, and others have found,[43] development of this film in a soft-working developer produces images of sharpness and grain superior to other fine-grained films. High Contrast Copy film has a practical speed of 12 when processed in POTA solution for 12 min at 75°F. The continuous-tone negative image has excellent sharpness and graininess with the ability to

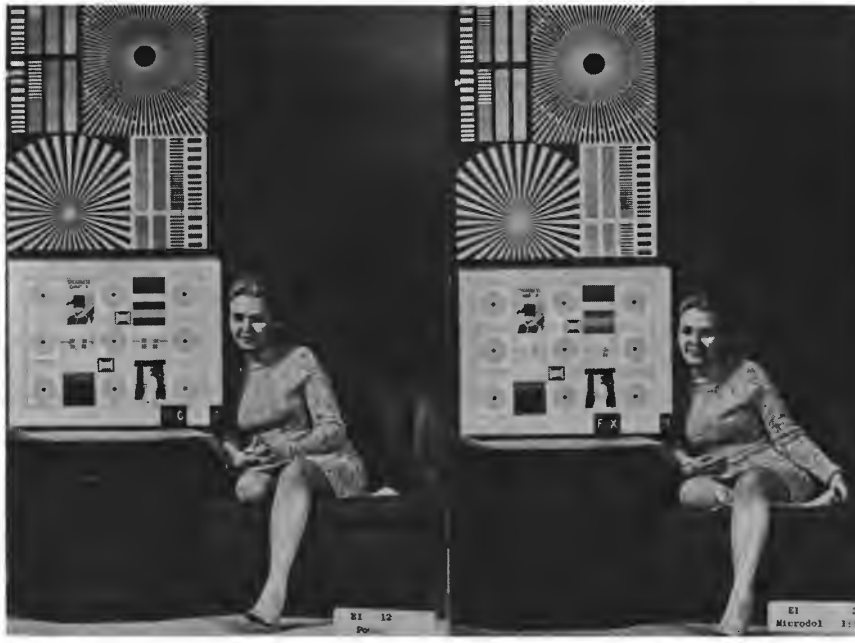

Figure 2. A comparison of image characteristics of Kodak High Contrast Copy film (left), exposed at ASA 12 and processed 12 min, 75°F, in POTA developer, with Kodak Panatomic-X film (right), exposed at ASA 32 and processed 11 min, 75°F, in Kodak Microdol-X developer, diluted 1:3. In the original prints at 25× enlargement, the lower graininess and greater sharpness of the High Contrast Copy film—POTA developer image were clearly evident. (John R. Altavena, Eastman Kodak Company)

render a wide range of exposure with detail in the shadows and highlights. (See Figure 2.)

HYPERSENSITIZATION AND LATENSIFICATION

The use of energetic developers to secure maximum emulsion speed represents one approach to the problem of increased film speed. The energetic developer, however, is limited because it still must distinguish between the unexposed crystals and those that have received some light exposure, however slight. Some of the very weakly exposed crystals will have sublatent images of a size below the threshold of developability for the developer in use. These sublatent images cannot be developed even by energetic developers, because the background fog level is very high when such an energetic developer must be used.

The possibility of building up the size of a latent image—that is, increasing its developability—or of increasing the size of the sublatent image sites to developable size has become an important concept in developing for maximum speed. Any treatment of the silver halide emulsion before exposure has been called hypersensitizing; any treatment of the emulsion after exposure but before development has been termed latensification (LATENt image intenSIFICATION).[44] In some cases the same treatment may be applied both before and then after exposure, so that the use of two terms for the same treatment is rather unwieldy. It is not uncommon to hear latensification used as a term to describe any means to secure more developable latent images.

Light-Exposure Treatment

Latent image is formed by light and the sublatent images by an inadequate level of light, so it is not unreasonable to use just enough more light to bring the inadequate latent images to a developable state. Very low levels of light may be used either before or after exposure, but usually this treatment is given after latent image exposure. Silver halide crystals with a latent image above a critical size as well as certain fog crystals will be reduced to metallic silver in the developer. Other grains may have started to form a latent image but of insufficient size to initiate development of the crystal. The purpose of a low, uniform second light exposure is to build these nondevelopable latent images to a size above the critical value for development. This second light exposure must not be of an intensity to make developable many of the remaining silver halide crystals that have not been exposed. Fortunately, the initiation of a latent image in an unexposed grain requires considerably more light than the reinforcement of a sublatent image of an inadequately exposed grain during the first exposure, but the level of fog may be increased by any additional light exposure.

The use of light latensification appears to be almost as old as photography itself,[45] but the use in 1927 by Eastman Kodak Company, according to R. H. Bomback,[46] represents an early application with modern film materials. In 1940 the Du Pont Film Corporation announced[47] that high-speed 35mm films could be increased from two to four times in speed by the deliberate fogging of the exposed film with a dark green safelight. Maximum latensification was obtained with a 25- to 40-min exposure at a distance of 10 ft from the safelight. Development was in any negative developer, but the time of development was extended from 50 to 75% to increase the contrast lost by the fogging exposure. Press photographers have been reported to attempt latensification of the film in the camera by making a second exposure of a

plain sky with the camera set at its highest shutter speed and smallest lens aperture.

The effect of low-intensity light exposure before or after a $\frac{1}{30}$-sec camera exposure on panchromatic films was studied by G. S. Moore.[48] Moore found that "an increase of threshold speed of the order of 2–4 times with only a slight reduction in contrast has been obtained when the fog increases to a value of 0.18–0.20 in 30 to 60 minutes." Speed increases reached a maximum with exposure times of 30 min, but contrast continued to increase with increasing exposure time. The latensifying effect was independent of the color of the light source. The speed increase did vary with the degree of development, the amount of the speed increase decreasing as the degree of the development increased.

Two developers were used by Moore to tray-develop panchromatic negative films at 65°F. The formulas for the MQ and Metol-pyrogallol formulations were as follows:

	No. 1	No. 2
Metol	0.67 g	4.4 g
Hydroquinone	2.7 g	—
Pryogallol	—	5.3 g
Sodium sulfite (crystals)	33.0 g	5.3 g
Potassium metabisulfite	—	5.3 g
Sodium carbonate (crystals)	33.0 g	81.0 g
Potassium bromide	0.27 g	2.1 g
Water to make	1.0 liter	1.0 liter

In his experiments Moore did not get the latensification effect when the low-intensity fogging exposure was given before the camera exposure. This failure was attributed by J. S. Friedman[49] to the fact that the fogging exposure must be at a level of fog (0.3 to 0.4 density units) approximately twice that given by Moore in his study. Preexposure light fogging must be sufficient to initiate latent image formation in unexposed grains, not just to make developable those already existing but not quite developable subimage specks of a latent image. Thus, as P. C. Burton and W. F. Berg[50] have pointed out in a study of latent image formation by a two-exposure technique, the low-intensity second exposure is enough to build up the already existing subimages to developable size but unexposed grains do not receive sufficient light intensity to build developable latent image. Postexposure flashing of

the film with infrared radiation has been patented as superior to visible-light latensification.[51]

Preexposure of photographic plates has been used by astronomers for the detection of extremely faint stars by long-time exposure. A short-duration light flash exposure, yielding considerable numbers of subimage latent image specks, is given just prior to image exposure. A simultaneous background-fogging exposure, yielding a density of 0.1 to 0.3, when added to the image exposure, increased the threshold sensitivity up to a factor of four for A. Guttman,[52] who used this technique. Simultaneous flash fogging exposures have increased the threshold speeds of aerial films up to eight times, but the flash exposure must yield fogs of 0.2 to 0.4 density unit for maximum effect.

Some modern high-speed negative film emulsions do not respond too favorably to a high-intensity camera exposure followed by a second low-intensity latensifying exposure. A uniform fog due to the second exposure may simply be imposed on the image produced by the first exposure. This occurs because the fogging exposure renders grains developable that had escaped the image exposure but the latent images of the initially exposed crystals were not increased appreciably. The increase in the film speed is very low.

If the high-speed photographic emulsion is desensitized sufficiently after the camera exposure, then the second light-fogging exposure would affect only those grains already exposed during the camera exposure. Subimages of the image exposure would be brought to a condition where they would develop. This desensitization-light latensification technique, devised by A. Hautot,[53] produced emulsion speed gains up to four times with the most modern negative emulsions; for example, Kodak Tri-X and P1200 emulsions developed 5 min in a normal Metol-hydroquinone developer or 11 min at 18°C in D-76 developer. Pinakryptol Yellow at a concentration of 0.15 g/liter was used for 5 min at 18°C for the desensitization after the camera exposure. With the P1200 emulsion, latensification after desensitization did not give results different than normal development in the energetic D-61A developer for $3\frac{1}{2}$ min at 18°C. Granularity, however, was higher for the development in the energetic developer than for normal MQ development of the emulsion that had been latensified after desensitization.

Three methods of securing maximum emulsion speed—(1) high-speed commercial developers, (2) forced development, and (3) light latensification—were compared by Paul R. Farber,[54] using 35mm Kodak Tri-X film, exposed to an average scene of 16:1 brightness ratio of highlight to shadow illumination. The shadow density reading of the fourth step of underexposure was used as a measure of the emulsion speed; a density of 0.05 above the density of the fog plus base density represents the value given by a film of ASA 400 exposure index. None of the developers showed any significant increase in this

shadow density of the fourth step of underexposure. Undiluted D-76 with 50 and 100% overdevelopment did not produce any increase in film speed over that given by normal undiluted D-76 development (7 min, 68°F). Only the image contrast was increased. Development in commercial developers such as Acufine ($4\frac{3}{4}$ min, 70°F), Diafine (2 min in bath A, 2 min in bath B at 75°F), or U.F.G. (undiluted for 1000 exposure index recommendation, $5\frac{1}{4}$ min at 70°F) either failed to increase the density of the fourth step of underexposure or actually decreased it.

Farber concluded, "Latensification seems to be the only process which actually increases emulsion speed." He achieved an exposure index of 800 for Tri-X film, thus doubling the rated film speed. After exposure at an exposure index of 800, the exposed film was unwound in the dark and taped to a wall, with the film emulsion facing away from the wall, at a distance of 10 ft from a safelight with a darkgreen No. 3 safelight filter and a 10-watt bulb. The film was given this low intensity exposure for 15 to 30 min, then developed normally in a developer recommended for it.

The use of low intensities of light to reinforce the subimage of a high-intensity exposure has been verified many times as a bona fide means to gain emulsion speed. The initial high-intensity image exposure produces much subimage, which then is built up with high efficiency by the second low-intensity exposure. The low-intensity exposure does not produce much subimage or developable image in virgin grains, so that the primary effect is upon only those grains initially exposed. W. F. Berg[55] concluded that the size alone, not the location of the subimage, was responsible for the behavior of the latent image produced by the initial high-intensity light exposure. Normal development of latensified film will provide normal contrasts, sharpness, and graininess. This is a distinct advantage over methods that attempt to achieve maximum speed by forced chemical development. Latensification techniques, however, have to be adapted to each photographic film, and a suitable developer must be selected, preferably by a scientific comparison. Even so, light latensification of an X-ray exposure did not produce any effect, so that latensification may be limited to the enhancement of the subimage formed by light exposure.[56]

Modern techniques of light latensification often add the light exposure during the actual camera image exposure. "Concurrent photon amplification" is the name given by Mel Cole to the use of four tiny lamps mounted in the camera chamber approximately 34mm in front of the film plane. As reported by Bob Schwalberg in the June 1976 issue of *Popular Photography*, Kodak Tri-X film (ASA index 400) could be exposed at ASA index 1600 to give top-quality results with normal development. So far, this procedure has been applied only to black-and-white films, but an overlay system called Colorflex has been proposed by Gerry Turpin for motion picture color

films [see *Camera*, **55** (2): 43 (1976)]. Colored light is reflected into the lens by a glass plate set at an angle in front of the lens. The overall color cast of the film is neutralized during printing. Turpin has claimed an effective speed gain of 5 stops (1600%) was possible with good color balance of the color film print.

Mercury Treatment

Daguerre founded photography with a process that used mercury vapor to physically develop the metallic silver latent image of a silver iodide plate. The atoms of mercury caused the physical size of the latent image to grow until the image became visible. Almost a century later—in 1928—K. Baukloh[57] found that mercury vapors could increase the sensitivity of modern silver halide emulsions. The practical use of this technique, however, was first emphasized by F. Dersch and H. Dürr[58] in 1937. Dry hypersensitization by mercury vapors was found to increase the speed of negative film emulsions about 50 to 150%, the exact increase depending upon the emulsion composition. X-ray films have been reported to either gain or lose speed, depending on the film type.[59]

Loose and unwrapped negative films were exposed to mercury vapors for 30 to 40 hours in the dark at room temperature. It is not at all necessary to unwind or unwrap tightly rolled film materials, as the mercury vapor will penetrate such materials with surprising uniformity, even tightly wound 1000-ft rolls of motion picture film. However, wrapped and spooled film materials will require from 7 to 10 days for the mercury-vapor treatment. The film should be placed in a container with a few drops of mercury and then the container sealed to prevent escape of the mercury vapors.

Metallic mercury should not be allowed to touch the film, as indiscriminate fogging will result. Mercury, both the metal and its vapor, is a poisonous element and should be handled with great care. Mercury vapors in the darkroom may cause other photographic materials to become unreliable because of unsuspected hypersensitization. In short, both the photographer and the photographic darkroom must be protected from exposure to metallic mercury or its widely permeating vapor. The solid mercury amalgams of silver, copper, tin, and zinc have been patented as effective but less toxic sources of mercury.[60]

Only the film sensitivity was reported to be changed by the mercury vapor treatment. The image contrast and the fog level remained the same. The spectral sensitivity is unchanged, so the filter factors for the film remain the same. Light latensification causes a change in the gradation in the film but mercury treatment does not, thus suggesting the use of the mercury treatment with color film materials. The speed increase is gradually lost during a period

of four weeks. The film speed is then slightly below the original speed and the fog level is lower. The film may be rehypersensitized with mercury vapors a second or even a third time.

The effect of mercury vapor upon the latent image is greater than upon the unexposed emulsion—that is, upon exposed film before development. The mercury treatment is the same as with hypersensitization. Film sensitivity was increased 100 to 150%. The increased effectiveness of the mercury treatment upon the exposed rather than the unexposed silver halide crystals was explained by Dersch and Dürr as follows:

> The effect of mercury upon photographic silver halide emulsions seems to be more closely related to the presence of metallic silver nuclei or photo-silver on the grains of ripened silver halide emulsion, rather than to the presence of silver sulfide. According to the present theories of the latent image, the metallic silver nuclei are of great importance to the developability of silver halide grains. However, these nuclei are not yet large enough to catalyze the action of the developer upon any particular grain. If the silver nuclei become larger, through the formation of more photo-silver by exposure or by prolonged ripening, the size of these nuclei, or the number of silver atoms, reaches or passes a certain critical point at, or beyond, which the nuclei can sufficiently catalyze, or accelerate, the reaction of the developer, and the grain thereby is rendered developable. This theory of the action of the silver nuclei and of the latent image has been very helpful in describing the peculiarities of the mercury vapor effect. It can be assumed that the silver nuclei absorb or adsorb mercury atoms, and possibly form silver amalgams. The size of the silver nuclei will become increased by these mercury atoms, which, in turn, could account for an increase of sensitivity of any particular grain. In case too much mercury is absorbed, the grain becomes developable without exposure, causing the emulsion to show fog.

When the mercury atoms escape from the silver amalgam on the grain surface, the sensitizing effect is lost.

Mercury treatment of both exposed and unexposed photographic materials, films and papers, has been the subject of a great deal of scientific experimentation. The effectiveness of the Dersch and Dürr treatment was confirmed, but considerable variability in results was reported. F. L. English[61] found that the effect of mercury varied with different manufactured brands of film emulsions, or different types of film by the same manufacturer, or different batches of the same emulsion type by the same manufacturer. Humidity at the time of treatment was found to be a factor in the final results. Sheppard, Vanselow, and Quirk[44] stated that with mercury latensification "to get reasonable precision (reproducibility) it was found necessary to condition the photographic layers to constant relative humidity, and to maintain the R. H. and the temperature constant. The conditions chiefly used were 50 per cent R. H. and 20°C and 75% R. H. and 24°C."

The long periods of mercury treatment of films might be considered a disadvantage. Dipping the film very briefly in heated mercury was said by U. Schmieschek[62] to be an effective means to shorten the time of mercury treatment, although running the danger of producing high background fog. A 50-sec immersion in mercury at 95°C yielded a threefold increase in emulsion speed of a Perutz panchromatic film. Greater speed gains—around four times—occurred with a 60-sec immersion at 105°C or a 40- to 50-sec treatment at 112°C. Gradation characteristics were changed and relatively high fog was obtained. The hypersensitization effect was lost rapidly, after only one day at 20°C. However, highly poisonous mercury vapors would be given off during the heating of mercury to such high temperatures, and escape of some fumes probably could not be prevented even with very careful handling.

The time of mercury vapor treatment may be shortened also by increasing the temperature and moisture. A 3-min mercury treatment at 125°F (50°C) of Agfa photographic paper followed by rapid cooling to room temperature was found by C. Rosetti[63] to give a result similar to many hours' treatment at room temperature. The hypersensitization of photographic films by mercury at 55 to 60°C for 1 hr gave approximately the same emulsion speed gain as keeping the emulsion at room temperature for one day in mercury vapors.[64] Glass plates were placed in a hermetically sealed glass desiccator with 3 to 5 ml of mercury in one cup and a small amount of water covering a surface area equal to 1 to 1.5 cm^2 in another cup. Optimum sensitization for Agfa Isopan ISS plates was obtained in 3 to 4 hours at 60°C. A 4-hr, 60°C treatment of these plates produced a sixfold rise in speed considered by the density threshold or a 2.4-fold increase when speed was measured at a density of 0.2 above fog. Reproducibility of the treatment was good. Maximum effect was achieved by hypersensitization rather than by treatment of the latent image of the exposed plates.

The speed increases achieved by hypersensitization were retained for several days when the plates were stored at 10°C. The greatest effect occurred at low densities, reducing the contrast slightly, but the speed increase was almost identical over the entire spectrum. An interesting observation was reported: "Chemically pure mercury washed with nitric acid had almost no hypersensitizing effect whatsoever. However, the external form and chemical composition of mercury was changed after prolonged heating of mercury and silver bromide plates or films in a desiccator." Analysis of a grayish-golden colored film on the liquid mercury surface indicated the presence of silver and bismuth, neither of which was present in the pure mercury sample. Mercury vapors amalgamate with silver atoms in the photographic emulsion during hypersensitization. During this treatment some of this amalgam apparently sublimes from the film, becomes a vapor, and precipitates on the liquid mercury surface upon cooling. It was concluded: "Mercury covered

with a film containing impurities appeared to be considerably more active in hypersensitization than pure mercury."

Possibly some of the increase in emulsion speed given by films in the presence of heated mercury may be due in part to the effect of the heat. Heating photographic emulsions has been found to give effective speed increases. In 1939 John G. Capstaff[65] secured a U. S. Patent on such a latensifying technique. He found that "submission of exposed and undeveloped panchromatic negative motion picture film to an atmosphere having a humidity of 80% and a temperature of 120° F for a period of four hours will result in a density of the silver image, after development, equivalent to an increase in speed of the emulsion of the order of from 50 to 60 per cent. Under these conditions, an increase of 25 per cent is noted after an hour's heating, and the increase continues rapidly for several hours and then more slowly, reaching a value of the order of 200 per cent at the end of twenty-four hours."

The effect of heating photographic materials was known long before Capstaff's patent. Extensive studies of heating dry plates, either before or after exposure, were reported by Hugo Maria Kellner[66] in 1926, to mention only one author. Kellner concluded that heating enhanced the ripening process of the photographic emulsion, increasing sensitivity, and was especially effective before or during exposure.

Other Gases or Vapors

The intensification of the latent image by sulfur dioxide was patented by Norwood Lee Simmons[67] in 1945. Sulfur dioxide gas, if not readily available, may be produced by adding a solution containing sodium sulfite to a dilute solution of acetic acid. When heated in a closed container, a solution of sulfuric acid (43.5 parts), sodium sulfite (10 parts), and water (100 parts) will also evolve sulfur dioxide. The exposed film may be first treated from 5 to 45 min in the sulfur dioxide fumes, then the film sealed in a closed container for about 48 hr, or the exposed film may be treated from 24 to 48 hr by the sulfur dioxide directly. Speed increases from 300 to 500% without noticeable increases in graininess were claimed. A multilayer color film after a 24-hr treatment gained the equivalent of one camera stop speed with no loss in color balance.

Latent image intensification with sulfur dioxide gas requires long treatment times. In U. S. Pat. 2,437,412, Walter J. Weyerts and Charles W. Wiederhold proposed to speed the treatment by "bathing an exposed silver halide emulsion layer, prior to development in an aqueous solution of sulfurous acid or a material which gives sulfurous acid in solution such as sodium bisulfite or potassium meta-bisulfite." After being bathed in a 1% solution of sodium

bisulfite or potassium meta bisulfite at a pH below 6 for 1 min, the treated film is allowed to stand in the freely circulating air of the darkroom from 10 to 20 min. The film is then developed in the normal manner.

A latent image produced by light may be increased by treating the exposed silver halide emulsion with the vapors of organic acids. This latensification method, originated by W. H. Mueller and J. E. Bates,[68] was said to produce film speed increases of 200 to 300% in the area of underexposure of high-speed emulsions. Only a small increase in fog, if any, was noticed. Treatment of unexposed photographic material usually resulted in a severe loss of photographic speed. A number of organic acids, such as acetic acid, formic acid, or propionic acid, were the most satisfactory. Oxalic acid has also been reported to be effective.[44] Strong inorganic acids, such as hydrochloric, hydrobromic, or nitric acid, should be avoided, as they attack the gelatin of the emulsion layer. Sulfurous acid, formed from sulfur dioxide gas dissolved in water, was also found to be an effective latent image intensifier, but the speed increase was 40 to 80% less than with acetic or formic acids.

The method of treatment consists of putting a few drops of the acid on a tuft of cotton, then inserting the cotton in a container with a close-fitting lid. In the dark the exposed film is placed in the container, out of contact with the cotton, and the lid sealed. With acetic acid, the treatment is completed within 1 to 2 hr. The film is then removed and developed normally but at once. Formic acid vapors were said to act several times more rapidly than acetic acid vapor or mixed vapors of these two acids. U.S. Patent 2,403,428 of Mueller and Bates[69] proposed that the organic acids in suitable solvents could be used as well.

The color sensitivity of panchromatic films was not altered by the acid treatment. Gradation is slightly flattened because of the increase in density due to the weakly exposed grains. Graininess is not increased unless the development time is extended 20% more than normal to raise the image contrast. The emulsion speed increase was held for two to three weeks, then declined to one-half this value after two months.

Other gases have been used to latensify photographic materials. Fuming with ammonia was practiced at the turn of the century. A mobilization of silver ions, in the form of $Ag(NH_3)^+$ ions, would allow the silver ion to be deposited on a subimage nucleus with the subsequent evolution of ammonia. Ozone, O_3, was reported to latensify negative photographic films resulting in speed increases up to 100%.[70] The degree of ozone latensification decreased as the completeness of the development increased. For complete development, no significant speed increase was obtained. This finding also supports the earlier work of T. H. James and W. Vanselow,[71] who concluded, "When energetic developers are used, therefore, latensification does not increase the number of developable grains but simply increases the rate at which some of

the grains develop." Thus, latensification by almost any method is most suitable for the fine-grain or low-activity developer, as the desirable graininess given by these developers would not be materially increased by the latensification treatment. If graininess is of no concern, the energetic developer would seem to be the simplest method to achieve maximum emulsion speed.

Solution Treatment

Solution treatment of photographic materials may be used to increase the emulsion speed. As Burt H. Carroll and Donald Hubbard[72] have noted, with some emulsions the "sensitivity to red light was tripled simply by washing out the soluble bromide" with water. The emulsion stability of commercial film products is maintained by excess halide ions, which act as a development restrainer. Hypersensitizing with solutions that remove the halide ion or increase the silver-ion concentration, although lowering the emulsion stability, is an effective means to increase the film speed. Treatment with ammonia solutions, or with ammonia solutions containing silver ions, produces an excess of silver ions over bromide ions in the emulsion, yielding increased emulsion speed.[73] One method of treatment involves a 1-min bathing in a 4% solution of 28% ammonia at 12°C or below.[74] Rapid drying in front of a fan is desirable. Speed gains of about three times were obtained for films given long exposures immediately after the treatment.

With Kodak IV-N emulsions, Edwin S. Barker[75] found "Speed gains of 14 to 20 can be realized by 3- to 6-min bathing in a water-alcohol solution containing 6% ammonia, at bath temperatures from 6° to 10°C, for exposure times of 5 min. Equivalent speed gains can be obtained by using pure water baths. However, if the alcohol is left out of the baths in the ammoniating procedure, the speed gains can be doubled."

The observation that the latent image may be intensified by the vapor or solution of hydrogen peroxide has been credited to Lüppo-Cramer.[76] Latensification by hydrogen peroxide or organic peroxides was found by by E. P. Wightman and R. F. Quirk[77] to be independent of the type of developer used. X-ray exposures were not latensified. *X*-ray exposures have been latensified, however, by using a 0.1% solution of thallium nitrate.[78]

Alkaline baths have also been used to latensify photographic materials. Bathing an exposed film for 1 min in a sodium perborate solution containing 2 g/liter of water has been reported[79] to double the emulsion speed. A 2% solution of triethanolamine was used for 1 min to hypersensitize exposures to both light and nuclear radiations.[80] Silver halide crystals are partially dissolved during the treatment, and silver is formed upon drying the emulsion, resulting in more effective sites for latent image formation. An ammonia-sodium carbonate hypersensitizing solution was reported[81] to yield the

Table 5. Mechanisms of Hypersensitizing and Latensifying Methods

Agent	Mechanism	
	Hypersensitizing	Latensifying
Light	(Crystallo)electronic	(Crystallo)electronic
Mercury vapor	Aggregation of metal atoms	Aggregation of metal atoms
Soluble silver salts	Mobilization of silver ions	Mobilization of silver ions
Weak organic acid	(No hypersensitization)	Mobilization of silver ions
Oxidants (peroxides)	(No hypersensitization)	Mobilization of silver ions
Ammonia and amines (and other alkalis)	Concentration of silver ions	Concentration of silver ions

greatest increase of film sensitivity given by a number of alkaline baths. Treatment was from 3 min up, followed by a 1-min rinse in methyl alcohol and rapid drying in air. This treatment was found superior to bathing in borax, ammonia-borax, sodium carbonate, or ammonia hypersensitizing solutions. The formulation contained 50 ml water, 50 ml methanol, 0.5 g sodium carbonate, and 4 ml 25% ammonia.

Table 5, from S. E. Sheppard, W. Vanselow, and R. F. Quirk,[44] summarizes the mechanisms of hypersensitizing and latensifying methods. The overall effect of hypersensitization and latensification is to lower resolution and to increase graininess. However, the gains in emulsion speed may produce results that are superior in graininess and resolution to other methods of achieving the same result.

A dilute solution of guanidine carbonate was used by Marilyn Levy[82] as a bath after exposure and before development to increase the effective speed of a photographic emulsion. The following is an example of the technique as illustrated in U. S. Patent 3,005,710:

A commerical photosensitive silver halide emulsion having an ASA exposure index rating of 650 is first exposed in the camera according to the desired increased speed rate. After exposure the film is placed in a 0.5 molar aqueous solution of guanidine carbonate of the formula—

$$2\,HN{=}C(NH_2)_2 \cdot H_2CO_3$$

for about ten minutes. The emulsion is then developed with or without rinsing in water in a developer for about ninety seconds, for instance, in an "Eastman Kodak" developer known in the trade as "D-72" having the following composition:

Water	cc	500
Elon (Mono-methyl para-aminophenol sulfate)	gms	3.1
Sodium sulfite (desiccated)	do	45.0
Hydroquinone	do	12.0
Sodium carbonate, monohydrated	do	80.0
Potassium bromide	do	1.9
Water to make 1.0 liter		

The film is then fixed, washed and dried.

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Chapter 11
Special-Purpose Developers

In photography, art and science go hand in hand. The development of a negative is just as important as the composition of the picture.

PHILIP M. CHANCELLOR[161]

LITHOGRAPHIC DEVELOPERS

Hydroquinone developers, usually of high alkalinity, have long been recognized for their unique ability to produce high-contrast photographic images. In 1901, for example, F. C. Lambert[1] recommended a hydroquinone-formalin-sodium sulfite developer to "the attention of process workers and others requiring strong contrasts with nearly clear glass for deepest shadows." Other early photographers[2] also recommended developers based on hydroquinone for applications involving photomechanical reproduction. A more recent type of high-contrast hydroquinone developer, called a lithographic or lith developer, is produced when the sodium sulfite content of the hydroquinone developing solution is maintained at a very low level. Contrasts produced on a suitable photographic film by such a developer are higher than obtainable by any other development method, particularly in regard to edge sharpness. (See Figures 1 and 2.)

Lith image development occurs in a distinctive manner. When a stepped exposure on a lith film is developed in a lith developer, only a very faint image of the steps with the greatest exposure is visible for a considerable period of the total developing time. Suddenly, as the step with the greatest exposure reaches a low density, a surge of developing activity sweeps across the step and completely blackens it. When each step in turn reaches this same initial density, the same form of accelerated development is repeated.

Lith development has been studied visually and recorded cinematographically by Hans Egger.[3] He compared two developers: (1) hydroquinone (2.5 g), sodium sulfite (0.5 g), sodium hydroxide (50 g), and potassium bromide (1 g) in a liter of solution, and (2) the same formulation with 20 g of sodium sulfite. With the low-sulfite formula he found that "After a certain period of time in which still nothing visible happens, part of the grains begins to develop very rapidly and starting from many centers. In this process, the shape of the grain remains intact to a large extent. The remaining grains develop considerably more slowly and mostly starting from a single nucleus, the grain becoming therefrom black all over. In many such experiments, it was also observed that in the first, the rapid phase, the reaction crosses over from one grain to the other neighboring grains."

When the developer contained 20 or 25 g sodium sulfite per liter of solution, there were no longer two phases of development. All grains started to develop at one or a few centers. The grains blackened uniformly over the whole surface and progressively became darker. No crossing over of the reaction from one grain to a neighboring grain was observed. Using a commercial lith developer (Agfa G8p), Egger found that the development took place with explosive violence with a speed unlike that of any other developer. The reaction spread from one grain into a neighboring grain and swept like a wave across the exposed film. Silver outgrowths from a grain triggered immediate reduction of any nearby grain they touched. The shape of the grains was distorted by the vigor of the reduction of the silver. The developed silver often assumed a multiple of the area of the original silver bromide crystals.

Lith development is interrupted after an optimal time of development to secure the highest contrast possible. The developing process produced by the low-sulfite lith developer is accelerated as compared with the development given by a similar hydroquinone developer of the same alkalinity but containing a greater amount of sodium sulfite—say, 20 g/liter. For most lith developers the optimum time of processing is from 2 to 5 min. Karl Frank[4] extended this development time to 15 min and found that the result was the same as that produced by development in a normal Phenidone-hydroquinone developer in a few mintues. The lith effect is completely lost unless the development is stopped at a critical time during the accelerated formation of the image. (See Figure 3.)

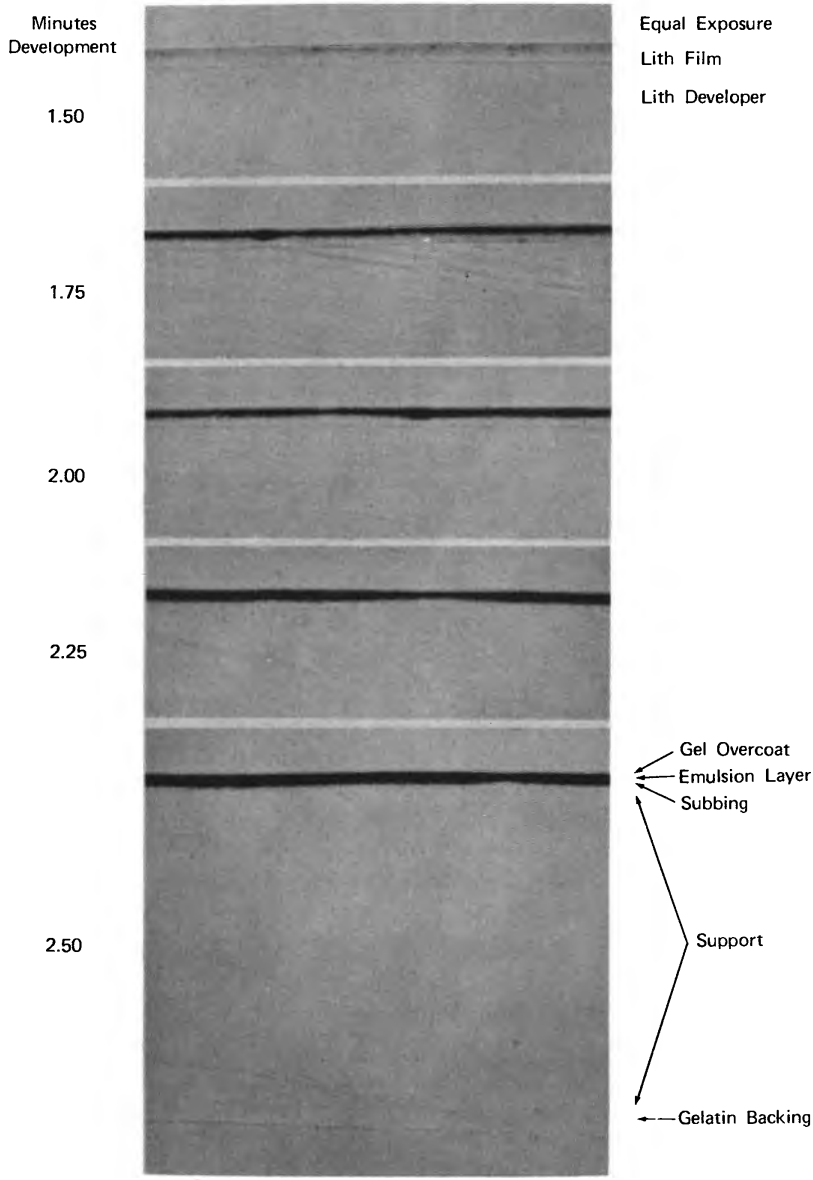


Figure 1. These cross sections of a lith film at 325 × magnification show the growth of density with increasing development time in a lith developer at a given exposure level of the film. The film base is in the lower part of each picture and is shown in its entirety in the lower photomicrograph. Note the irregular distribution of silver in the image, especially in the earlier stages of development. (James King and Grant Haist, Eastman Kodak Company)

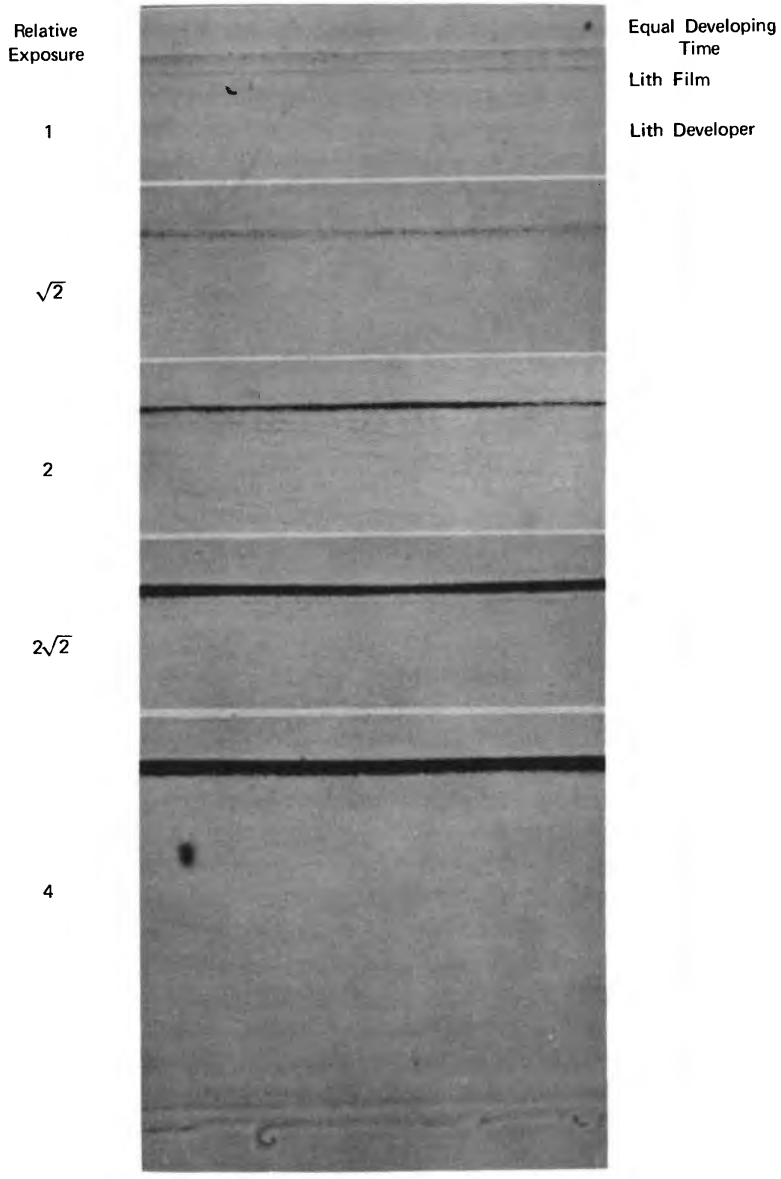


Figure 2. The growth of density at equal developing time in a lith developer is shown for increasing exposure of a lith film in these cross-section photomicrographs (325×). The entire film structure is shown in the lowest photomicrograph. Development time was 3 min, 68°F. (James King and Grant Haist, Eastman Kodak Company)

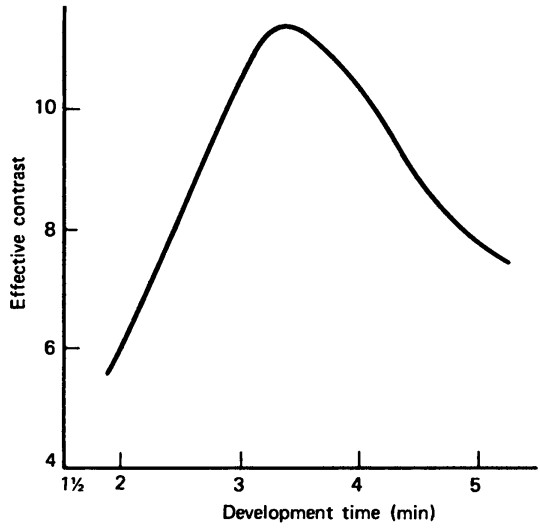


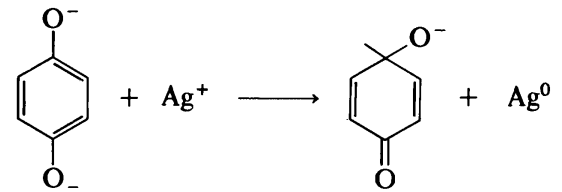
Figure 3. The effective contrast given by lith development of a lith film rises rapidly to a maximum, then decreases. [D. A. Pullen and M. C. Lloyd, *Printing Technology*, 14 (2): 69 (1970)]

The Mechanism of Lith Development

Probably the first complete explanation of the lith effect was given by J. A. C. Yule.[5] Yule reported that "The experimental evidence shows that (a) developer in the immediate neighborhood of developing grains is more active than fresh developer; (b) this extra activity is very short-lived and is followed by the lowered activity characteristic of exhausted developer; and (c) the extra activity is destroyed by sulfite ion." By the time the developer with the enhanced activity has diffused about 0.1 mm from the initial site of development, the more active developer will have lost this activity and will act like any other exhausted developer.

The activated developer is an oxidation product of hydroquinone that is short-lived and is inactivated by sodium sulfite. The surge of blackening of an exposed area after a period of little activity may be explained by the following mechanism:

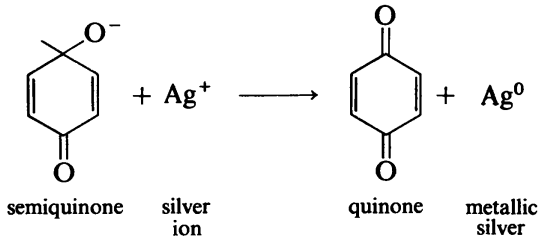
(1)



hydroquinone dianion | exposed silver | semiquinone | metallic silver

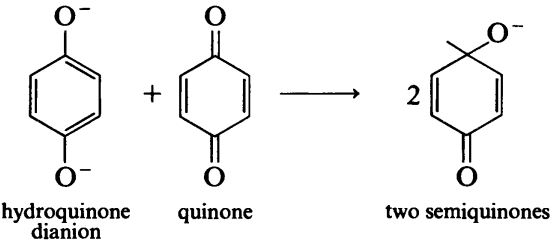
The dianion of hydroquinone loses one electron to a silver ion, producing metallic silver and the semiquinone of hydroquinone. This is a slow reaction that occurs at the beginning of development by hydroquinone.

(2)



The semiquinone is in a very unstable electronic state, and this free radical reacts quickly with another silver ion to produce metallic silver. The semiquinone is converted into the more stable quinone molecule. Note that this reaction would occur much more quickly than the formation of the semiquinone from the hydroquinone dianion.

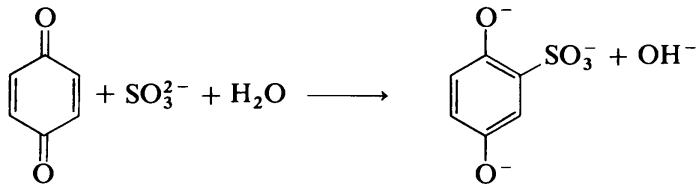
(3)



Quinone is a very reactive molecule in alkaline solution and takes one electron from a hydroquinone dianion, producing two semiquinones. This is a very rapid reaction. Thus, once very small amounts of the oxidized forms of hydroquinone are produced, during that period of lith development that produces a just-visible density, the ensuing reactions proceed autocatalytically at a very rapid rate to produce semiquinone. The semiquinone gives up an electron very easily to form the more stable quinone, so it is capable of developing silver that would require a longer time in a normal hydroquinone developer. Once this buildup of semiquinone reaches a certain level, development rapidly goes to completion, producing the blackening of image areas so characteristic of lith development.

The presence of sodium sulfite to any great degree acts to remove the semiquinone or the quinone. The rapid accumulation of the highly active semiquinone is prevented, and the semiquinone never reaches a level sufficiently high to influence the rate of development. The removal of quinone

by sulfite results in the formation of hydroquinone monosulfonate, a developing agent of less activity than hydroquinone itself. This reaction occurs as follows:



quinone sulfite ion water hydroquinone monosulfonate anion hydroxyl ion

As the semiquinone diffuses outward from a developing silver halide crystal, it will trigger any exposed crystal into complete development. This accelerated developing action does not spread very far laterally, because the sulfite ion in the developer will react readily with the semiquinone. The sulfite level of the developer must be controlled very carefully, as too little sulfite will permit aerial oxidation of the developer without producing a true lith type of accelerated development, and too much sulfite will remove the semiquinone and quinone before the acceleration of development can build up to give a lith effect.

It has been suggested by J. E. LuValle[6,7] that hydroxyhydroquinone, rather than the semiquinone proposed by Yule, is the accelerating substance in a low-sulfite hydroquinone developer. However, Karl Frank[4] failed to detect any hydroxyhydroquinone in his investigations. It was also pointed out by J. Q. Umberger[8] that the addition of hydroxyl ion to quinone, forming the trianion of hydroxyhydroquinone, is only one-hundred millionth as fast as the reaction between quinone and dianion of hydroquinone to form two semiquinones.

Umberger found that

in sulfite-containing hydroquinone solutions of pH 9.0 and less, development results principally from the monoanion, HQ^-. The HQ^- concentration is roughly 1000 times greater than Q^{2-}, in the pH range specified, and thus predominates in the development in spite of the greater specific activity of Q^{2-}. Thus, the data suggest an "electron-transfer barrier" as alternate to the past "charge-barrier" rationalization of development induction. High contrast results from semiquinone formed in the development reaction; this radical quickly gives off its proton to assume the more stable, resonating anion-form which is an active developer free from "electron transfer barrier." In low-sulfite hydroquinone solutions, e.g., the formaldehyde-containing "litho" developers described above, the contrast is particularly high due to the local accumulation of quinone and the active Q^- (semiquinone).

The role of radicals containing an electron with an unpaired spin, such as semiquinone, may be monitored directly during the active development of a coated emulsion by the use of electron spin resonance (ESR) spectroscopy.[9,10] The ESR spectrograph has been used to provide unambiguous identification of the semiquinone of hydroquinone when exposed lith films were immersed in low-sulfite hydroquinone developers in the cavity of the spectrograph. The semiquinone was produced within the emulsion layer, not in the solution of the developer. After exposure of the lith film, a slight induction period was noticed at the beginning of the development, followed by the detection of a burst of semiquinone, rising to a maximum concentration in 15 to 30 sec, then decreasing. A high-contrast image was produced on the film. When excess sodium sulfite was added to the lith developer, the semiquinone growth and decay were not observed, and the lith film developed a lower-contrast image. The interpretation of the ESR observations may most easily be explained by using the Yule hypothesis of lith development. A possibility still exists that an oxidation product of the hydroquinone may actually be enhancing the activity of the hydroquinone by aiding in the electron transfer from the hydroquinone dianion to the latent image silver–silver halide interface on the surface of the silver halide grains.

Frank[4] observed that additives that remove oxygen from a sulfite-free hydroquinone developer promote the lith effect but quantities of sodium sulfite above 2 g/liter destroy the lith effect. (See Table 1.)

Both surface and internal latent images are formed when the silver halide of a lith photographic material is exposed. The lith developing solution with its low concentration of sodium sulfite has almost no solvent effect on silver halide, so that only the surface latent image can be developed. Quinone, formed during lith development, is a known oxidizing agent and is capable

Table 1. Effect of Developer Additives on Lith Effect

Developer Stock Solution	Additive	Lith Effect?
Hydroquinone, 18 g/liter	Oxygen present	No
Sodium carbonate, 60 g/liter	Oxygen absent	Yes
Potassium bromide, 2 g/liter	Sodium sulfite (>2 g/liter)	No
	Sodium sulfite (<2 g/liter)	Yes
	Hydroxylamine	Yes
	Hydrazine	Yes

Source: From Karl Frank.[4]

of bleaching surface latent image. Such a bleaching action would be most pronounced in the areas of low exposure, yielding greatly increased image contrast. T. H. James[11] has concluded, "The reactions of quinone with gelatin and with latent image may be of more importance to the lith development effect than the reaction with hydroquinone to form semiquinone." He has postulated that

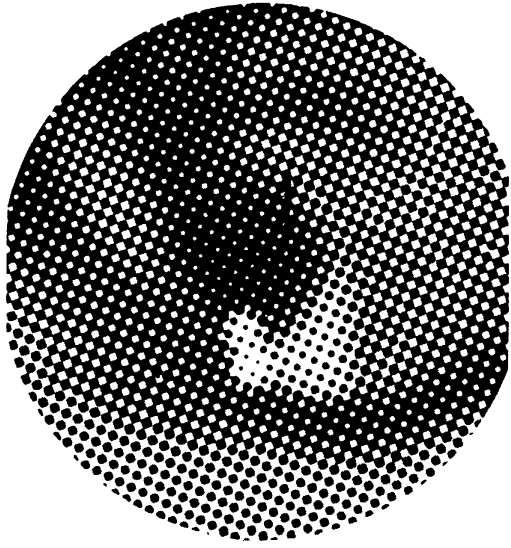
A *large* acceleration of development is not required to give the lith effect. The combination of a moderate increase in rate of development of some grains and the suppression of development of other grains with smaller latent-image centers would suffice. These conditions could be provided in practice by the reaction of quinone with the gelatin, leading to accelerated development of some grains by the "superadditive" mechanism, and the retardation of development of less exposed grains in the surrounding areas by oxidation of the latent image. The oxidation could be partial or complete, and could be effected by quinone or semiquinone, acting in concert with halide ions supplied by the active development of grains in the more highly exposed areas.

Figure 4. Photographs to be reproduced by printing are usually photographed through a lined screen on lith film. The image is broken into dots of various sizes. (*a*) The dot pattern of a fine screen is often not evident, as in this reproduction of a photograph, but the dot structure of the circled areas is revealed by magnification (*b*). (Eastman Kodak Company)

Studies of the characteristics of lith development by Tsuneo Suga[12,13] have also considered the possibility of quinone bleaching of the latent image during development. The presence of bromide ions was found essential for this to occur. Suga[14] concluded that in the presence of bromide ions at lower pH the oxidized forms of hydroquinone formed during development destroy the latent image in the low exposure region. This effect coupled with accelerated development of the latent image in the high-exposure regions provides the line and dot sharpness so characteristic of only lith development. (See Figure 4.)

The Lith Photographic Emulsion

The dense, sharp lines and dots given by lith development require the use of a special lith photographic emulsion. The first lith film seems to have been conceived in commercial secrecy, as this writer has been unable to determine who first originated the lith system of film emulsion and developer. Analysis of commercial lith films has indicated that the emulsion is essentially a



(b)

Figure 4. (*continued*)

chlorobromide one, with chloride about 60 to 90%, with a few percent or less of iodide, the rest being bromide. According to Tsuneo Suga,[15] "The chlorobromide emulsion is suitable for lith development, because it has a high developability by hydroquinone and its latent image in the lower-exposure regions is easily oxidized by quinone. In the case of chloride emulsion the latent image in the lower-exposure regions is hardly oxidized. This is the fact that probably diminishes its lith effect. Low developability of bromide emulsion may yield little lith effect. The sulfur sensitized chlorobromide emulsion has the balancing of developability and of oxidizability suitable for lith effect. Low oxidizability of latent image of the sulfur-gold sensitized emulsion diminishes lith effect. Low developability and low oxidizability of the gold sensitized emulsion yield no lith effect." High-quality lith films have been made, however, with sulfur-gold sensitized chlorobromide emulsions.

The classic lith photographic material has contained a cadmium chlorobromiodide emulsion. A Steigmann[16] states:

> By leaving out the cadmium in this emulsion it will easily be recognized that cadmium ions activate the digestion, triple the speed in the blacks, and improve the gradation if the same digestion time is given as in the case of the cadmium containing emulsion. The litho emulsion (with cadmium) is also pre-eminently suited to illustrate the great importance of the chemical ripening restrainers of gelatin which are removed by the so-called "alum clarification" processes. Without these restrainers it is impossible to obtain the extremely vigorous gradation which is required from litho emulsions that are developed in paraformaldehyde-hydroquinone developers. The restraining egg albumen plus minute traces of tetraalkylthiuram monosulphide can turn an inert alum clarified and carbon-treated gelatin which works by itself much too soft (for litho emulsions) into a litho type gelatin.

Steigman has given the following as the composition and method of making a lith-type photographic emulsion:

Solution I

Water	425 ml
Concentrated hydrochloric acid	2 ml
Cadmium chloride, $CdCl_2 \cdot 2H_2O$	0.4 g
Gelatin	20 g
Egg albumen, 10%	2–3 ml

Solution II

Water, distilled	100 ml
Silver nitrate	20 g

Solution III

Water	40 ml
Cadmium chloride, $CdCl_2 \cdot 2H_2O$	0.3 g
Sodium chloride	7 g
Potassium bromide	1.5 g
$Na_3RhCl_6 \cdot 18H_2O$ solution (1:10,000)	4 ml

All solutions at 55°C.

Add solution II to solution I rapidly with stirring. Follow at once with solution III. Add 12 ml of potassium iodide solution (1:500). Digest for 60 min at 60°C. Add 0.3 g of magnesium oxide. Follow with 3 g of silver nitrate in 30 ml of water. Add 12 ml of Rr 340 solution (1 : 4000). Precipitate with 150 g of anhydrous sodium sulphate. Cut the precipitate. Rinse. Give three changes of distilled water, 1 liter each within about 1 hr—i.e., every 20 min. Dissolve to 250 ml. volume. Add 5 g of gelatin. Soak, then digest at 60°C to maximum speed and gradation using litho developer. (Takes about 45 min or longer if lower temperature is used which may be preferable.)

Other metal salts have been added to the solutions for the preparation of the silver halide emulsion. Iridium, cobalticyanide,[17] and iron compounds[18] have been patented for this use in lith emulsions. The incorporation of at least 10 g of a cadmium salt per mole of silver in the silver halide emulsion, either in the emulsion layer or in a contiguous layer, is said to minimize the uneven image development given by continuous transport processing machines.[19]

Most metal salts have serious drawbacks, such as toxicity, which poses a pollution problem. Desensitization of the low-exposure areas of a photographic material can be accomplished by inclusion of polyethylene oxides, such as polyethyleneglycols or their esters,

$$HOCH_2CH_2O(CH_2CH_2O)_nCH_2CH_2OH$$

when n is from 7 to 200 units. Molecular weights are usually in excess of 1500. These compounds had originally been used by Ralph Kingsley Blake and Walter Dewey Baldsiefen[20] and others[21–24] to improve the speed and contrast of photographic silver halide emulsion layers. This major discovery was, in part, responsible for some of the characteristics of modern photographic films. Another discovery was the fact that polyethyleneoxides, in either the emulsion or the developer or both, depressed the activity of developing solutions containing only hydroquinone as the developing agent. The net increase in image contrast was beneficial for lith images of lines and dots, where edge sharpness is critical. This increase in contrast was found to

occur only with lith-type emulsions whose development is interrupted at the moment of maximum image gradation as is done during lith development.

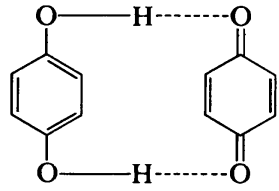
A variety of compounds have been added along with the polyethyleneoxides: A 3-pyrazolidone developing agent,[25] tetrazaindenes and thioureas,[26] polymeric vinyl compounds (for improved dimensional stability),[27,28] quaternary ammonium salts,[29] and pyrazolones.[30,31] Large amounts of formaldehyde in the emulsion have been claimed to permit more sodium sulfite to be present in the developer.[32–34] Block copolymers,[35,36] polyureas and polyurethanes,[37] and pentaerythritol phosphoric acid esters[38,39] have been patented as replacements for the polyethyleneoxides. It is evident that modern lith emulsions are much more complex in composition than the early types.

Composition of the Lith Developer

The practical lith developer is a hydroquinone solution of moderate alkalinity and low free-sulfite-ion concentration with potassium bromide as the restraining agent. Only hydroquinone and an alkali are absolutely essential to yield the lith effect. Quantities as small as 0.5 g/liter of a second developing agent, such as Metol or Phenidone, can destroy the high contrast normally given by the hydroquinone alone. Potassium bromide is beneficial in securing the highest-contrast image, but its presence is not necessary to observe lith development. Benzotriazole and 5-methylbenzotriazole are also effective.[40] The free sulfite ion must be very low in the solution, making lith developers so unstable that mixing from two solutions just before use often is necessary.

Sulfite-free developers containing 0.005 *M* hydroquinone, 0.95 *M* potassium hydroxide, and 0.0067 *M* potassium bromide in oxygen-free nitrogen atmosphere were reported by T. H. James[41] to produce the characteristic high contrast of lith development. Chlorohydroquinone, bromohydroquinone, toluhydroquinone, and *p*-hydroxyphenylglycine were also found to yield a lith-type development but of a lesser contrast than given by hydroquinone. In the presence of a small amount of sodium sulfite, other mono-substituted hydroquinone derivatives, such as butyl, propyl, methyl, or sulfophenyl hydroquinone, have given very high contrast. The 2,3-dimethyl, 2,5-dimethyl, and 2,6-dimethyl derivatives of hydroquinone failed to give the lith effect for H. Zwicky.[42] Frank[4] reported that 2,5-dimethylhydroquinone-3-sulfonic acid, even in the presence of 60 g/liter of sodium sulfite, produced "satisfactory lith development." High contrasts have not been obtained from developers containing various catechols, aminophenols, or ascorbic acid.

Quinhydrone is the name given to a developing agent consisting of the chemical union of a molecule each of hydroquinone and quinone.



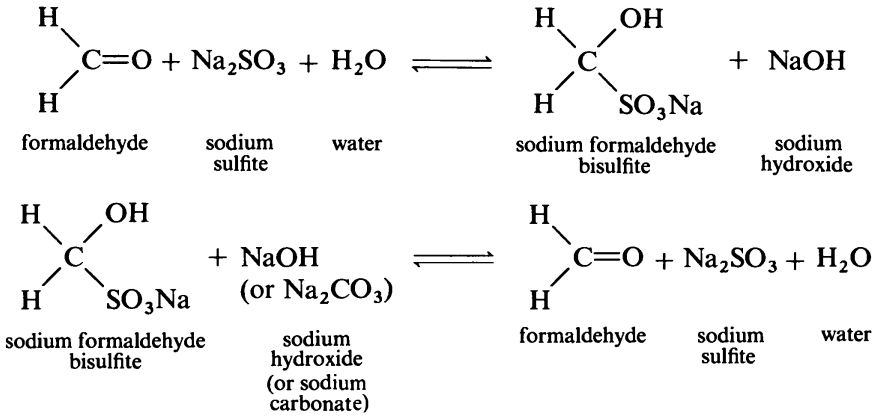
quinhydrone

When used without sulfite, quinhydrone produces appreciable concentrations of semiquinone in solution. A one-use developer, prepared from 4 g quinhydrone, 1 g benzotriazole, and 20 g sodium hydroxide in 1 liter of solution was compounded by N. M. Zyuskin and E. Yu. Braichevskaya,[43,44] who found that the sulfite-free solution was stable for 15 to 20 minutes. A Russian positive film yielded very high contrast with a 7-min development. Fog was not formed, but the film was stained yellow. The yellow color may be reduced by a 5-min treatment in 5% sodium hydrosulfite before washing the film. Optimum quinhydrone concentration was found to be 2 to 3 g/liter of solution.[45]

The high contrast of the lith effect is obtained at moderate alkalinity with lith films or certain photographic papers. At pH of 13 or higher, even positive film materials will show the effect. As the pH of the developer is increased, the amount of sodium sulfite may be increased from the optimum of 1 to 2 g/liter at moderate alkalinities. However, the maximum contrast is less at very high alkalinities. The most suitable conditions for lith development occur at a pH of 10 with low sulfite at 1 to 2 g/liter and a small amount of 0.5 to 1.0 g/liter of potassium bromide to act as a restrainer. The presence of potassium bromide, sometimes with or without benzotriazole or 5-methylbenzotriazole in small quantity, lengthens the time of optimum development. Thus, lith developers producing images of maximum contrast are the result of carefully balancing low sulfite concentration with sufficient restrainer in a hydroquinone solution around pH 10. Increased bromide concentration may permit 3 to 5 g/liter of sodium sulfite to be used, but the contrast of the image is somewhat less than for the low-bromide, low-sulfite formulation.

An alkaline lith developing solution with 0.5 to 2.5 g/liter of sodium sulfite quickly loses developing activity because the loss of the sulfite allows the oxidation of the hydroquinone. A higher concentration of sulfite cannot be used without impairing the lith effect. One way to maintain the sulfite at the optimum level is through the use of certain aldehydes and ketones that combine with the sodium sulfite to form addition compounds. Formaldehyde sodium bisulfite is such a "sulfite ion buffer." Formaldehyde is an irritating gas and difficult to handle. A solid polymeric form of formaldehyde

called paraformaldehyde was originally combined with sodium bisulfite or potassium metabisulfite to form the bisulfite complex in water solution.[46] Paraformaldehyde is difficult to dissolve. Sodium formaldehyde bisulfite, a water-soluble and odorless compound, was suggested and patented for use in lith developing solutions.[47,48] In aqueous alkaline solution this compound comes apart or dissociates to yield formaldehyde and sodium sulfite.



The extent of the dissociation of an aldehyde-bisulfite compound depends on the alkalinity of the solution. At the pH of 10 of lith developers, most of the sulfite is held in the addition compound and is not available for reaction. Only about 3 to 6% sodium sulfite is free from the addition compound. As this sodium sulfite is used up, a sufficient amount of the aldehyde-bisulfite compound comes apart to maintain this concentration of free sulfite ion. Developers containing sodium formaldehyde bisulfite have solutions whose oxidation life is considerably greater than developers containing an equivalent amount of free sodium sulfite. Adding sufficient free sulfite to match the oxidation life of the developer with the formaldehyde bisulfite causes the lith effect to be lost. The use of addition compounds with sulfite serves the dual function of maintaining a sulfite reserve, a "sulfite buffer," to maintain a low sulfite concentration as well as yielding superior keeping properties over a nonbuffered low sulfite developer.

Usually, sodium formaldehyde bisulfite at 30 to 70 g/liter is the compound used as the sulfite buffer. However, many other bisulfite compounds have been studied for this purpose. Acetaldehyde sodium bisulfite, cyclohexanone sodium bisulfite,[49] glutaraldehyde sodium bisulfite, glyoxal sodium bisulfite, and acetone sodium bisulfite[50] are examples of addition compounds found to be of value for lith developing solutions. In some cases two of these compounds may be used in combination.[51] Cyclohexanone sodium bisulfite was claimed by Richard W. Henn[49] to be a superior antioxidant for lith devel-

opers. Using a solution containing 5 g hydroquinone, 25 g sodium hydroxide, and one liter of water, the following comparative results were obtained:

Compound	Concentration (g/liter)	Time to Darken
Sodium sulfite	2	50 min
Acetaldehyde sodium bisulfite	4	95 min
Acetone sodium bisulfite	5	95 min
Methyl ethyl ketone sodium bisulfite	8	75 min
Ethyl acetoacetate sodium bisulfite	8	80 min
Cyclohexanone sodium bisulfite	20	Over 4 hr
Methyl cyclohexanone sodium bisulfite	20	Over 4 hr

Each developing solution was exposed to air, and the time taken to darken was a measure of the effectiveness of the antioxidants.

The use of sodium formaldehyde bisulfite in commercial preparations has caused lith developers to be prepared from two parts or two solutions. Such a formulation is given in British Patent 643,411:[52]

Solution A

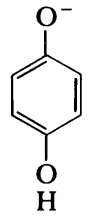
Sodium formaldehyde bisulfite (monohydrate)	136.5 g
Hydroquinone	57.0 g
Boric acid (crystals)	7.6 g
Sodium bisulfite (dry)	12.0 g
Ethyl alcohol (95%)	110.0 ml
Water to make	1.0 pint

Solution B

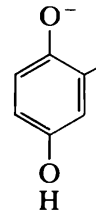
Potassium carbonate	189.00 g
Boric acid (crystals)	23.70 g
Potassium bromide	2.84 g
Water to make	1.00 pint

To make the working solution, three pints of water are added to each of solutions A and B. The two resulting solutions are then added together to make four quarts of the developing solution at pH 9.9 to 10.1.

Sodium formaldehyde bisulfite, the compound that has been commonly used in lith developing solutions, is an inefficient sulfite-ion buffer because its dissociation constant is too low. In addition, in alkaline solution, even in the absence of oxygen, this sulfite-ion buffer and hydroquinone have been reported to react, causing the loss of the active developing agent, an increase in the free-sulfite-ion concentration, and a lowering of the solution pH. According to R. L. Childers,[53] these changes are the result of the following reactions:



$+ [HCHO + HSO_3^-] \longrightarrow$

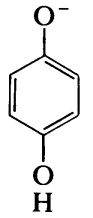


$CH_2OH + SO_3^{2-} + H^+$

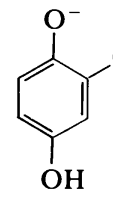
hydroquinone anion | formaldehyde bisulfite ion | 2-hydroxymethyl hydroquinone anion | sulfite ion | hydrogen ion

The dissociated formaldehyde bisulfite may continue to react with the hydroquinone anion until the other three ring positions are also hydroxymethylated.

The formaldehyde bisulfite ion may also react to form sulfomethylated products.



$+ HO—CH_2—SO_3^- \longrightarrow$



$CH_2SO_3^- + H_2O$

hydroquinone anion | formaldehyde bisulfite ion | 2-sulfomethyl hydroquinone anion | water

The sulfomethylation may continue until all the ring positions of hydroquinone have been filled. A combination of hydroxymethylation and sulfomethylation may occur on the same ring. Some of the possible 20

derivatives have been detected in aged lith developers. Childers concluded that "The loss of activity with incubation keeping of developers formulated with higher than normal levels of formaldehyde bisulfite or formaldehyde indicates that hydroquinone reacts more readily with formaldehyde than with formaldehyde bisulfite ion."

Substitutes for bisulfite addition products have been sought. Such a replacement should remove a low level of the semiquinone and, if possible, protect the developing solution against the effects of aerial oxidation. Two compounds may be used to accomplish these two needs. Ascorbic acid has been detected in commercial lith developers for some years and has been recently patented as the antioxidant.[54,55] Three grams of sodium sulfite and 3 g of ascorbic acid were used in a liter of solution containing 12 g of hydroquinone and 2.6 g of potassium bromide with sufficient sodium carbonate monohydrate to give a pH of 10.05. Hydrazine at 5 g/liter, hydroxyl ammonium chloride at 5 g/liter or hydroxylamine have also been used as protectants for lith developing solutions. Mercapto-containing organic compounds are known to react with semiquinone and act as antioxidants. Cysteine, for example, in Japanese Patent 57304/66, was claimed for use in lith developing solutions.

The relative amounts of antioxidant needed on a molar basis to achieve the same oxidative stability as sodium sulfite in hydroquinone solutions were determined by Christina Lazaridis[162] as follows:

Antioxidant	Relative Amount Required
Sodium sulfite	1
Ascorbic acid	3
N-Methylhydroxylamine hydrochloride	4
4-Chlororesorcinol	6
Malononitrile	6
2-Methylresorcinol	6
3,6-Dihydroxypyridazine	10
Meta-cresol	10

According to U. S. Patent 3,772,022,[56] "ascorbic acid is, however, poor in stability and hence tends to be decomposed. Particularly, ascorbic acid is readily decomposed when metal ions such as iron ions or copper ions are present, and this leads to the poor stability of the developing solution.

Further, ascorbic acid has the disadvantages that the progress of the development is slowed to a certain extent and that the dot quality is reduced when it is added in a large amount." It was claimed that nitrile compounds, such as acetonitrile or malononitrile, increase "remarkably" the storage stability of a lith developing solution without any adverse effect on dot quality. The following lith developer

Sodium carbonate monohydrate	50 g
Formaldehyde sodium bisulfite	45 g
Potassium bromide	2 g
Hydroquinone	18 g
Sodium sulfite	2 g
Acetonitrile	10 g
Water to make	1 liter

was used for $2\frac{3}{4}$ min at 20°C to develop a lith film "comprising a film support having coated thereon a silver chlorobromoiodide emulsion composed of 70 mol% AgCl, and 0.2 mol% AgI sensitized with gold and sulfur, spectrally sensitized with 3-carboxymethyl-5-(2-(3-ethylthiazolinilidene) ethylidene) rhodamine, and containing polyoxyethylenenonylphenyl ether having 50 ethyleneoxide groups, mucochloric acid and polybutylmethacrylate." Better solution aeration and dot quality were obtained by this solution than with a similar developer with 1.0 g of ascorbic acid replacing the acetonitrile.

The presence of boron compounds has been used to lengthen the useful life of lith developers containing formaldehyde bisulfite. Boron compounds, such as boric acid and sodium metaborate, were used in the early lith developers.[47,48] A U. S. Patent by Laurence G. Welliver and Jerry S. Krizka[57] contained specific examples of preferred formulations, such as

Hydroquinone	15.0 g
Formaldehyde bisulfite	50.0 g
Sodium carbonate	20.0 g
Sodium metaborate	20.0 g
Potassium bromide	1.5 g
Water to make	1.0 liter

This developing solution was said to remain 8 hr in an open tray without deterioration due to aerial oxidation.

Kojic acid was claimed by George Schwarz[58] to be superior to boric acid in lith developing solutions. Improved tray life was said to result when

Table 2. Lith Developer Formulations

Ingredient	Unit of Measurement	Kodak D-85	Pako Lith Developer	Du Pont 7-D
Water (about 90°F or 30°C)	ml	500	500	500
Hydroquinone	gram	22.5	12.0	45.00
Sodium sulfite (anhydrous)	gram	30.0	3.0	60.0
Potassium metabisulfite	gram	2.6		5.0
Boric acid (crystals)	gram	7.5		15.0
Potassium bromide	gram	1.6	2.6	3.0
Paraformaldehyde	gram	7.5		15.0
Sodium formaldehyde bisulfite	gram		25.0	—
Sodium carbonate monohydrate	gram		23.0	—
Ascorbic acid	gram		5.0	
Water to make	liter	1.0	1.0	1.0
Dilution				1:1
Development time (min at 68°F)		$1\frac{1}{2}$–$2\frac{1}{4}$	2	2

10 g kojic acid was present in one liter of solution containing 40 g of sodium formaldehyde bisulfite, 25 g hydroquinone, 38 g sodium carbonate, and 2.0 g potassium bromide.

Lith developer formulations are summarized in Tables 2 and 3.

Lith Developers for Machine Processing

Lith materials have usually been processed in trays, sometimes with a minimum of agitation. Lith developing solutions have a high sensitivity to the bromide and hydroquinone concentrations as well as being sensitive to pH changes.[59] Lith developers exhibit adjacency effects due to local exhaustion of the developing agent or accumulation of bromide ions. Yet, beginning in the early 1960s, automated processing of lith film was started, using roller transport machines that accepted single sheets of film. Some of the problems in automated lith film processing have been outlined by L. T. Connolly.[60] Trying to adapt the unstable lith developing solution to a machine resulted in uneven image development identified as drag lines, loss

Table 3. Two-Solution Lith Developers

Ingredient	Unit of Measurement	Du Pont 15-D	Ansco 79b	Chemco Dev
Solution A				
Water (125°F or 52°C)	ml	500.0	750.0	750.0
Hydroquinone	gram	45.0	90.0	135.0
Sodium sulfite (anhydrous)	gram	30.0	120.0	
Sulfuric acid	ml	4.0	—	
Boric acid (crystals)	gram	—	30.0	
Potassium bromide	gram	—	6.0	
Potassium formaldehyde bisulfite monohydrate	gram		—	110.0
Diethylene glycol	ml			118.0
Ethylenediamine tetraacetic acid	gram			0.26
Potassium hydroxide	ml	—	—	2.8
Cold water to make	liter	1.0	3.0	1.0
Solution B				
Water (125°F or 52°C)	ml	500.0	750.0	
Sodium carbonate (anhydrous)	gram	30.0		
Potassium carbonate	gram	90.0		
Sodium hydroxide	gram	—	—	9.5
Potassium bromide	gram	8.3	—	1.57
Sodium sulfite (desiccated)	gram	90.0	1.0	
Paraformaldehyde	gram	—	30.0	
Potassium metabisulfite	gram	—	10.5	
Potassium formaldehyde bisulfite monohydrate	gram	—	—	63.0
Boric acid	gram	—	—	13.5
Cold water to make	liter	1.0	1.0	1.0

Table 3. (*continued*)

Ingredient	Unit of Measurement	Du Pont 15-D	Ansco 79b	Chemco Dev
Dilution		1:1	3:1	1:1 + 4 parts water[a]
Development time (68°F) (constant agitation)		4 to 5 min	2 to 3 min	

[a] The working solution of this developer (U. S. Patent 3,162,534) when it begins to show exhaustion is said to be substantially revived when 15 ml of the following solution is added: sodium sulfite, 116 g; potassium hydroxide (45% in water), 256 ml; water to make 1 liter.

of contrast due to developing agent exhaustion during the crossovers between processing solutions, and general loss of developing activity due to deterioration with time. Connolly states that most of these difficulties have been surmounted but offers no information on the nature of the film or processing solutions.

During machine processing, the lith film spends a considerable amount of the developing time passing from one tank to the next. The developing agent in the high-exposure areas is quickly exhausted but the developing agent continues to be active in the areas of low exposure. The image contrast is lowered by this form of undesirable compensating development. Increased effective contrast, the elimination of drag lines, and improved speed were said to result if the lith film contained a gelatin overcoat of at least 130 mg of gelatin per square foot. According to Kirby Mitchell Milton,[61] "The heavy overcoat layer provides the material during processing with an ample supply of unexhausted developer or other processing solution while the material is not actually immersed in the processing solution such as occurs when the material is travelling through the air or other gaseous medium while being transferred from one processing tank to the next. Many difficulties previously encountered are thus overcome, for example, the occurrence of drag lines is virtually eliminated." A lith film emulsion containing 85 mole percent chloride, 0.1 to 5.0 mole percent iodide, and the rest bromide, containing a dispersed polymerized vinyl compound, has been said to be particularly adapted for machine processing in continuous-transport machines.[62]

A lith developing solution for use in such continuous-transport processing machines has been described by Thomas J. Masseth.[63,64] The solution

contained hydroquinone or a hydroquinone derivative as the developing agent, a carbonyl bisulfite-amine condensation product, and at least 0.075 mole of free amine per liter of developing solution. An example of such a solution (pH 9.5) contained

Sodium-*bis*(2-hydroxyethyl)-aminomethane sulfonate*	82.0 g
Sodium sulfite	3.0 g
Boric acid	7.5 g
Hydroquinone	22.5 g
Potassium bromide	1.6 g
2,2′-Iminodiethanol	39.0 g
Water to make	1.0 liter

Lith Developers Containing Polyethylene Oxides

Polyethylene glycols, especially those containing at least nine —CH_2CH_2O— groups and their mono- and di-aliphatic carboxylic acid esters, shorten the induction period of MQ developers, yielding increased emulsion speed and improved contrast.[65] However, when polyoxyalkylene ethers of hexitol ring dehydration products[66] or polyethylene glycols[67] were added to lith developers, there was a restraint of development in the low-exposure areas of a lith film, resulting in greatly increased contrast without a gain in the fog level. Improved dot quality was also obtained, but the repressed development caused a loss of emulsion speed. For example, these effects were obtained when Carbowax 4000, a product of Carbide and Carbon Chemical Corporation, at 1 g/liter, was present in a hydroquinone lith developer with 2.5 g sodium sulfite per liter (pH 10.1). Polymeric derivatives of polyoxyethylene and polyoxypropylene have also proven effective in lith developing solutions.[68–70]

The development rate is slowed when lith film is developed in the presence of a polyethylene oxide or other suitable polymeric compound. Development accelerators are often added to the emulsion to overcome this difficulty.[71] Arginine hydrochloride added to the emulsion layer or the developing solution has been reported to shorten the induction period of lith development without destroying the high contrast given by the lith developing solution.[72–74] Quaternary ammonium salts, in admixture with the polyethylene glycol in the emulsion, have been said to give "increased contrast and improved dot quality when used for recording screened images."[75]

* Sodium formaldehyde bisulfite and 2,2′-iminodiethanol can be used to form this compound in situ.

Often, a polymeric compound is present in both the emulsion and in the developer—for example, *N*-vinyl-2-pyrrolidone in the emulsion layer and polyethylene oxide in the developing solution.[76]

Modern lith materials and solutions have been greatly changed by the use of polymeric materials in both the film emulsion and the developing solution. The effect of polyethylene oxides (PEO) on the suppression of development by hydroquinone has been studied extensively. H. W. Wood[77,78] found that PEO did not influence the diffusion of developer components but that "PEO interferes in some way with the accumulation of semiquinone development catalyst at the grain surface." P. J. Hillson[79] concluded that the retardation of development by hydroquinone was "explained by the inability of the developing agent to penetrate the adsorbed layer of surfactant and develop the underlying emulsion grains." Many investigations of the mechanism of the polyethylene oxide effect in photographic emulsion and developer have been carried out by Russian scientists.[80–94]

TANNING DEVELOPERS

The accelerated rate of development given by low-sulfite lith developers is just one photographic use of the very reactive intermediates formed by the oxidation of a developing agent. The partially or completely oxidized forms of some developing agents react readily with the gelatin surrounding a crystal of silver halide undergoing reduction. The gelatin molecules are bridged by the oxidized developer molecules, causing this modified gelatin to be less water soluble and to have a much higher softening temperature. These changes are very similar to those that occur during the process of tanning leather, which decreases the solubility of the long protein molecules by the formation of chemical crosslinks between the protein chains. Photographic developers which cause the gelatin to become less soluble in the vicinity of developing silver halide grains are called tanning developers because of the similarity of their action to that of tanning of leather.

Images produced by tanning developers, after removal of the soluble gelatin in the undeveloped areas, consist of gelatin which varies in thickness in proportion to the intensity of the light exposure of the photographic emulsion. The relief image so formed is often called a matrix, and the unhardened photographic film is commonly called matrix film. Although processing methods are available for exposing matrix film from either the emulsion side or the film base side, it is much easier if the film is exposed through the film base. In this case, the insolubilized gelatin is attached directly to the base, and only direct development by a suitable tanning developer is necessary. After image development, the unexposed, undeveloped areas of the matrix film are dissolved away with hot water, leaving a relief image representing the original light exposure. (See Figure 5.)

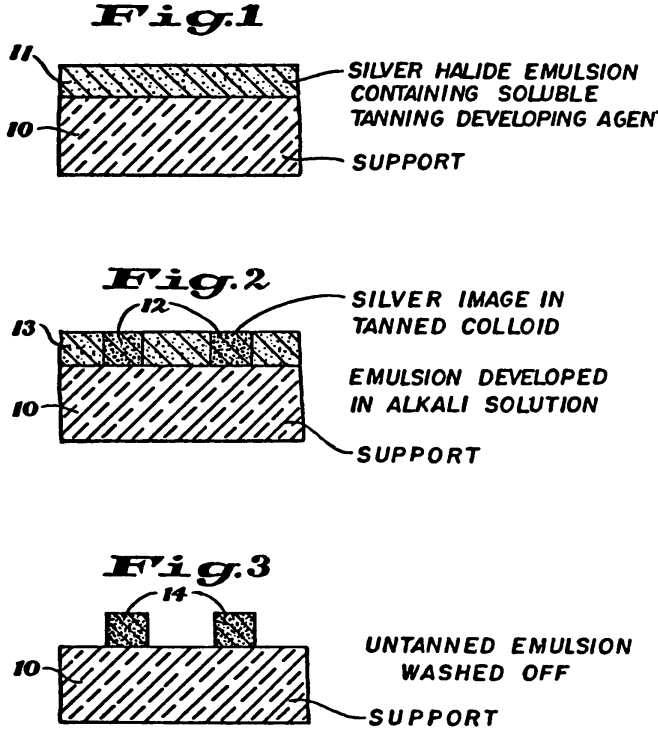


Figure 5. These figures in U.S. Patent 3,300,307 of A. C. Smith, Jr., illustrate the formation of a gelatin relief image (Fig. 3) after activation (Fig. 2) of a silver halide emulsion containing a tanning developing agent.

Although this method of processing with tanning developers is the most common, other methods have been devised. The unhardened, exposed photographic material may first be treated with a nonhardening developing solution, then the remaining silver halide flashed to light and developed in a tanning developer to harden the gelatin in the regions of the second exposure. The original exposed areas are removed with hot water, leaving a positive relief image. Another technique involves exposure of the photographic material through its transparent support, development in a tanning developer, and then, instead of the usual hot water wash, a transfer of the unhardened gelatin to a second support. The transferred image is utilized as a positive. For some printing purposes the hardened and unhardened images may differ enough in ink receptivity that they may be left together on the same support.

Contact-diffusion hardening development has been suggested by G. I. Loznevoi.[95] The exposed photographic material is brought into intimate contact with a flexible support containing an unhardened gelatin layer

impregnated with a tanning developing solution. The tanning solution migrates to the exposed layer, reducing the silver and producing products that harden gelatin. Some of these products migrate back to the original unhardened gelatin layer and harden it in proportion to the degree of exposure of the photographic material. The gelatin layer is then treated with hot water to form a gelatin relief image. A tanning developing agent must be used that has oxidation products that are capable of diffusing a considerable distance before reaction with the gelatin. The relief gelatin image may, however formed, be used to imbibe dyes which, when brought in contact with another gelatin-coated film or paper base, usually containing a compound to attract and hold the dye, will transfer the dye to the receiver material. If three matrices are made from suitable separation negatives representing blue, green, and red sensitivity and the matrices are used to transfer yellow, magenta, and cyan imbibition dyes, in exact register, a three-color picture will be the result. This is the technique used in the Kodak Dye Transfer Process for the making of color prints on paper (still a standard of quality by which color prints are judged) and in the Technicolor Imbibition Process for the production of release color motion picture film for theater use.

Applications of Tanning Development

These modern dye transfer processes appear to have had their origin in 1879, when J. W. Swan[96] patented the use of a pyrogallol-ammonia developer without sodium sulfite to produce relief images on photographic plates useful for printing processes. One method for producing relief was to place the developed plate in water of about 90°F to cause the parts not acted upon by the light to swell more than the tanned image areas. However, Leon Warnerke[97–99] appears to be the first, according to British Patent 1436, April 1, 1881, to dissolve or etch away in warm water the parts of the image that were not developable in the sulfiteless pyrogallol-ammonia developer. The insolubilized gelatin relief image containing the developed silver image was left attached to the surface of the emulsion support.

Early tanning developing solutions were used to form a transfer printing plate.[100] The concentration of sodium sulfite was used to control the degree of hardening. A suitable formula was

Water	251.4 ml
Pyrogallol	0.7 g
Metol	0.6 g
Potassium bromide	0.3 g
Sodium carbonate	13.0 g
Sodium sulfite	2.6 to 3.9 g

Potassium iodide at 1.3 to 5.8 g in the above formula was said to produce a less contrasty image.[101] After tanning development, the emulsion is fixed to remove the unexposed silver salts, the unhardened emulsion is removed with hot water, and then the developed silver is oxidized—that is, bleached—to convert it into silver salts that can be removed. A combined bleaching and fixing solution is described in British Patent 187,638:[102]

Solution A

Water	3.0 liter
Copper sulfate	454.0 g
Ammonia	364.0 g
Water to make	3.8 liters

Solution B

Sodium thiosulfate	454.0 g
Water to make	3.8 liters

Use one part of solution A with three parts of solution B.

Pyrogallol tanning developers need to be activated by alkali, yet they cannot contain much sulfite, as this preservative destroys the tanning action. Pyrogallol developers containing sodium hydroxide tend to harden both the exposed and unexposed gelatin of the emulsion layer. Pyrogallol developers containing ammonium hydroxide are satisfactory except for the difficulty of securing uniform results because of the variation in the strength of the ammonium hydroxide. Leonard T. Troland proposed to add sodium hydroxide and ammonium chloride to provide greater image uniformity.[103,104] According to Troland, "The sodium hydroxide and ammonium chloride react to some extent to form sodium chloride and ammonium hydroxide; and better results seem to be attained by separately adding the sodium hydroxide and ammonium chloride just before use." A developer consisting of 0.82 g pyrogallol, 0.02 g citric acid, 0.40 g potassium bromide, 0.34 g sodium hydroxide, 0.17 g ammonium chloride, and enough water to make 100 ml was used to process motion picture film on a continuous machine. The citric acid was included for its preservative action before the developer was mixed; the potassium bromide was added to act as a development restrainer.

Relief images were used to absorb dye and produce motion pictures in color by imbibition printing.[105,106] The Technicolor Motion Picture Corporation was the early leader in this difficult technique. Although the

silver need not be removed, the relief image sometimes was grainy and lacked resolving power. Another difficulty was "breakthrough" in the highlights; that is, the gelatin was too thin to absorb sufficient dye. These difficulties were said to be overcome by the invention described in a patent issued to Technicolor:[107]

In one aspect the present invention involves a method of forming a dyed relief record from a colloid layer sensitized with the silver-halide which comprises exposing the colloid layer to form a latent image, developing the colloid layer to form a silver image and hardening the colloid layer in the region of the developed silver, etching off the unhardened colloid to form a relief record, and dying the relief record, characterized by using hypo in the developer to prevent the layer from being etched all the way through in the highlights. Preferably the developing and hardening is effected in the same stage by using a pyro developer. Any substantial amount of hypo is beneficial up to the region of 2% to 3%. With a pyro developer best results have been obtained with approximately 2%.

The formula of such a pyrogallol developer was listed as

Calgon	1.00 g
Sodium sulfite	0.60 g
Pyrogallol	3.00 g
Metol	2.49 g
Potassium bromide	2.00 g
Sodium thiosulfate penthydrate	20.00 g
Sodium carbonate monohydrate	150.00 g
Water to make	1.0 liter

Development was for 2 min at 64°F. After this, the matrix film was treated for 1 min in a 0.3% solution of acetic acid, then etched for $1\frac{1}{2}$ min in water at 140°F to remove the areas of unhardened gelatin.

E. J. Wall, who was directly concerned with compounding tanning developers for motion picture uses, concluded from his experiments that

It seems immaterial whether ammonia or one of the fixed alkalis are used, though the latter are preferable for color work, as they give more uniform results than the volatile ammonia. The actual composition of the developing solution seems also to be of no particular moment, only such good results have never been obtained with any reducing agent as with pyrogallol.

There are one or two points to which attention should be directed. One is that the total omission of sulfite is apt to give a superficial skin of insolubilized gelatin, that may later give a little trouble. The second and more important point is the absence of fog. Fog is metallic silver, and as the deposition of silver is accompanied by insolubilization

of the gelatin, it is clear that a foggy result will not develop into so good a relief as a plate that is clean. Therefore, it is advisable to use a fair amount of bromide in the developer and to allow for this in the exposure, as it is well known that bromide slows the plate, to use a current phrase.

These and other observations are given in Wall's book, *The History of Three-Color Photography.*[108] An excellent discussion of transfer processes is also given in Chapter 26 of Joseph S. Friedman's book, *History of Color Photography.*[109]

Increasing the Stability of Tanning Developing Solutions

An antioxidant, such as sodium sulfite, can be used only in very small quantities in a tanning developer, because this preservative destroys or limits the tanning action if more than about 2 to 3 g/liter are present. Tanning developing solutions are unstable, making mixing from two solutions before use a necessity. The developer is discarded after use. An early patent of Charles W. Bennett[110] proposed to use borax to stabilize the solution against air oxidation and acetone to maintain a strong chemical activity of a catechol tanning developer. Ascorbic acid or isoascorbic acid or their salts have been recommended as antioxidants for tanning developing solutions.[111] A suitable tanning photographic developer had the composition

Sodium sulfate	150 g
Catechol	8 g
Potassium bromide	1 g
L-Ascorbic acid	4 g
Water to make	900 ml
Sodium hydroxide (10% solution)	100 ml

According to British Patent 862,615,[112] the use of ascorbic acid in tanning developers has many drawbacks:

First, ascorbic acid is unstable in alkaline medium which results in a strong decrease of the anti-oxidizing action. Further it has been found that after exposure and development of a photographic element in a tanning developer to which ascorbic acid was added as anti-oxidizing agent, the relief image, on removing the non-developed unhardened gelatin, is insufficiently hardened and is either completely or partially washed away by the warm water. This occurs in particular when relatively large quantities of ascorbic acid—which owing to the instability of ascorbic acid in alkaline medium are necessary to keep the tanning developer operative for a sufficiently long period—are added to the developer.

This phenomenon can be explained as follows: ascorbic acid itself is a developing substance and competes as such with the tanning developing substance. Since the oxidation products of ascorbic acid do not harden gelatin, the hardening is insufficient on the exposed areas where the ascorbic acid has likewise formed black silver by competition with the tanning substance. As a result, the exposed areas which are developed, but insufficiently hardened by the ascorbic acid, are either completely or partly dissolved by the warm water on eliminating the unexposed gelatin parts which are thus unhardened in development.

Ascorbic acid borates, unlike free ascorbic acid, were claimed to eliminate these deficiencies. They were stable in alkaline medium and do not compete with the tanning developing substance. Potassium salt of isoascorbic acid borate at a concentration of 5 g was added to a solution containing 6 g catechol and 30 g sodium carbonate anhydrous in a liter of water to produce a tanning developer giving sharp negative relief images.

Kojic acid or its salts has been claimed to produce tanning developing solutions that have superior keeping properties.[113] Calcium or magnesium precipitates from hard water may be avoided if the kojic acid is dissolved first in the water before the other developer ingredients are added to the water. Kojic acid was also said to protect the developing solution against the reduction of the sulfite to sulfide by microorganisms that might be present in the water. A tanning developing solution comprised

Catechol	5 g
Sodium sulfite (optional)	3 g
Potassium carbonate	30 g
Kojic acid	10 g
Water to make	1 liter

The Mechanism of Tanning Development

The mechanism of the tanning action was studied in 1896 by A. Haddon and F. B. Grundy,[114] who found that the insolubilization of gelatin was due to the action of the oxidation products of a number of developing agents, including hydroquinone, that occurred simultaneously with the development of exposed silver of the photographic emulsion. Later, in 1906, A. and L. Lumière and A. Seyewetz[115,116] showed that gelatin could be insolubilized in the absence of silver halide if a pyrogallol-sodium carbonate solution was allowed to oxidize in air. After standing in air, alkaline solutions of hydroquinone, catechol, diaminophenol hydrochloride, diaminoresorcin hydrochloride, Metoquinone, Adurol, Metol, and Eikonogen caused the insolubilization of gelatin. Para-aminophenol, para-phenylenediamine, and Glycin

caused no insolubility. In closed containers none of the developing agents caused insolubilization of gelatin; in the presence of 3% sodium sulfite, only pyrogallol and diaminophenol hydrochloride produced gelatin insolubility. Other phenolic compounds, such as gallic acid, tannin, alpha-naphthol, beta-naphthol, resorcinol, phloroglucinol, and dihydroxynaphthalene, also were found to insolubilize gelatin in alkaline solutions subjected to aerial oxidation, but often the oxidation took many days.

These early studies established that the oxidation products of a large number of compounds, some incapable of being photographic developing agents, were able to insolubilize gelatin. Much more recently R. B. Pontius[117] suggested that for developing agents to be satisfactory for tanning development these reducing compounds must have "(1) the presence of one or more functional hydroxy groups, and (2) the possession by the developer of a reasonably good photographic reduction potential." Those developing agents producing quinone or quinoneimine upon development usually were active tanning agents. All developing agents were classified into three categories: strong, weak, or ineffective.

Strong	Weak	Ineffective
Pyrogallol	Amidol (2,4-diamino-phenol)	Glycin (*N*-carboxy-methyl-*p*-aminophenol)
Catechol	Metol (*N*-methyl-*p*-aminophenol)	*p*-Phenylenediamine
Hydroquinone	*p*-Aminophenol	Most derivatives of *p*-phenylenediamine
Aminocatechol	Ortol (*N*-methyl-*o*-aminophenol)	
Aminopyrogallol	Eikonogen (1-amino-2-hydroxynaphthalene-6-sulfonic acid)	
Chlorocatechol	*o*-Aminophenol	
Chlorohydroquinone	Ascorbic acid	
Bromohydroquinone		

Combining a developing agent with a compound which is a tanning agent and possibly having developing activity as well may increase the effectiveness of the tanning development. The combination of Metol with pyrogallol was mentioned in an early patent[118] and has been of continued interest since that time. In his studies of the addition of Metol to tanning agents of various kinds, R. B. Pontius[117] found that the Metol-pyrogallol or Metol–tannic acid developers were especially effective in promoting a strong tanning development. The Metol-pyrogallol developer gave considerably greater "speed" of the relief image than the developer with pyrogallol alone. How-

ever, combining pyrogallol with hydroquinone or Glycin caused a loss in "speed."

The ease of oxidation of the auxiliary agent determines whether the pyrogallol developer gives more or less "speed" of the relief image. For example, Metol, Amidol, and *p*-aminophenol are more easily oxidized by silver bromide than is pyrogallol, but pyrogallol is more readily oxidized by silver bromide than by hydroquinone, Glycin, or *p*-phenylenediamine or its derivatives. The quinonoid products produced by the developing action of Metol, Amidol, or *p*-aminophenol can then promote the oxidation of the pyrogallol, enhancing the tanning activity. On the other hand, pyrogallol produces oxidation products from silver promide development that may react with hydroquinone, Glycin, or the *p*-phenylenediamines, resulting in a loss of oxidized pyrogallol that tans the gelatin.

Metol, a weak tanning agent alone, is an active developing agent whose oxidized forms can cause tanning development by an auxiliary agent which may not even be a developing agent. This interaction between compounds is the reason that gelatin tanning occurs when Metol is combined with either tannic or gallic acids, which are not active developing agents. The addition of Phenidone to a pyrogallol or catechol developer appears to operate in a similar manner, considerably increasing the rate of tanning development.

The possibility of using controlled cross oxidation is thus suggested as a means to increase tanning development. The Troland process used exposure to air or a bath of potassium ferricyanide just after the surplus developer was washed off but before the untanned gelatin was etched away.[119] A. G. Tull[120] reported that "provided supplementary oxidation was given, almost any developing agent could be used alone under suitable pH conditions to give a tanned image." Following development of 2 min in 2.5 or 5.0 g developing agent with 2.5 g sodium hydroxide in a liter of water and a 1-min water rinse, the oxidizing bath of 10% potassium ferricyanide was used for one-half minute, followed by the wash-off step in hot water. Under these conditions only Glycin, Phenidone, and *p*-phenylenediamine failed to give a relief image. A substituted *p*-phenylenediamine, such as *N*,*N*-diethyl-*p*-phenylenediamine hydrochloride, did exhibit tanning action. Tull then reported that he used a variety of oxidizers, as shown in Table 4, following development by (1) Amidol, (2) 2-amino-5-diethylaminotoluene, or (3) caustic hydroquinone with sodium sulfite—for example, Kodak D-8 Developer. Some oxidizers were more effective than others, but no form of oxidation would produce relief images following a strongly sulfited developing solution unless the oxidizer was a bleach which itself tans gelatin when it oxidizes.

According to Tull's study, "The degree of tanning arising during development is not chemically equivalent to the mass of silver reduced but is observed to vary from developing agent to developing agent. It also varied when

Table 4. Effect of Oxidizers on Gelatin Relief Image Formation

Oxidizer	Relief Image Given by Developers Containing		
	Amidol	2-Amino-5-Diethyl-Aminotoluene	Developer D-8
Potassium ferricyanide	Very heavy relief	Weaker relief	No relief
Dichromate tanning bleach	Very heavy relief	Relief	Good relief
Copper chloride	Good relief	No relief	No relief
Mercuric chloride	Relief of excessive contrast	Relief	No Relief
Farmer's solution	Fair relief	No Relief	No relief
Permanganate/ sulfuric acid	Very weak relief	Fair relief	No relief
Iodine in dioxane	No relief	Fair relief	No relief
Cupric bromide/ sulfuric acid	No relief	No relief	No relief
Water with 5 min aeration	Strong relief	Faint relief	—
Hydrogen peroxide	Strong relief	Faint relief	—
Dilute nitric acid	Faint relief	No relief	—
Ferric nitrate	Strong relief	Good relief	—

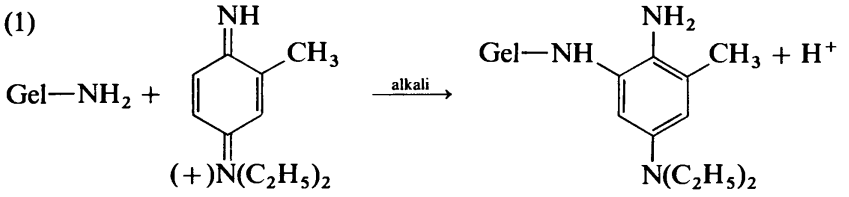
pH of the bath is changed or when developing agent concentration is changed, and even when proceeding from shorter to longer exposures. The departure from a constant relationship of relief and silver is probably attributable to side reactions such as stain formation in which the oxidation products are not wholly utilised in combining with gelatin."

Stain image formation is distinct from the formation of a tanned relief image. Stain results from two or more developer molecules reacting together in an oxidizing medium to yield a colored, insoluble product that is retained, imagewise, in the gelatin. Sodium sulfite inhibits staining, except incompletely in the case of pyrogallol developers, by combining with the oxidation products, but gelatin tanning is inhibited. Gelatin tanning occurs when the oxidized developer molecule reacts with a gelatin molecule in an oxidizing medium. Reaction of the coupling developer molecule may occur so that only one end of the molecule is attached to a gelatin chain, the other end being free

but near other gelatin molecules. In this case of a latent tanned image, a posttreatment in alkali, such as sodium carbonate, or a potassium ferricyanide solution, results in the attachment of the free end of the developer molecule to a nearby gelatin molecule. This crosslinking between the two gelatin molecules given by oxidizing posttreatments after tanning development increases the relief image speed.

A possible mechanism for the reaction of a gelatin molecule with a free $-NH_2$ group in a side chain (denoted in the equations by Gel$-NH_2$) was proposed, yielding a latent tanned image (1) which is then oxidized (2) to form crosslinked gelatin molecules (3) of the tanned image.

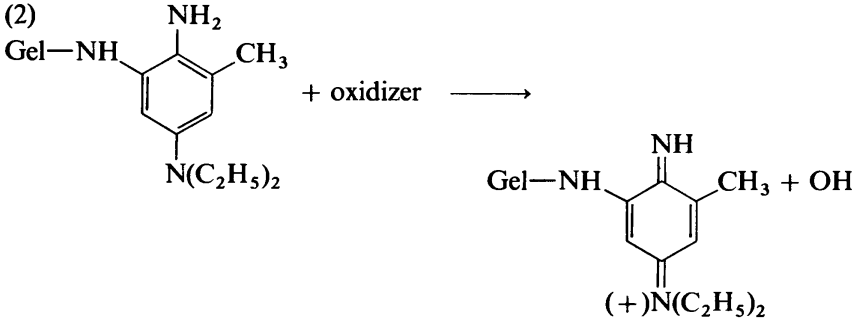
(1)



oxidized form of developing agent

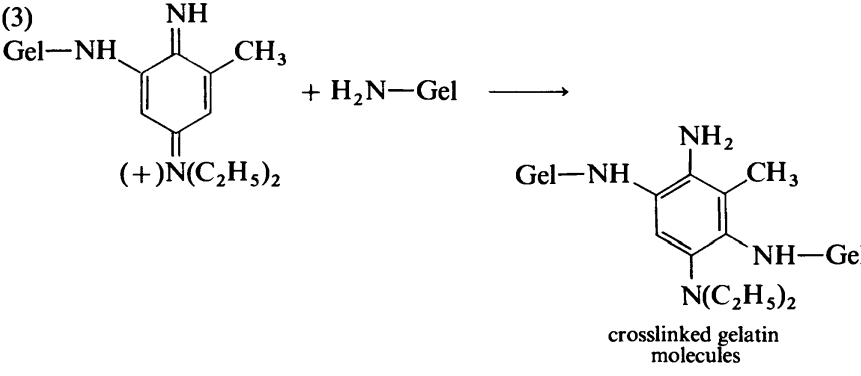
first gelatin compound in latent tanned image

(2)



oxidized form of first gelatin compound

(3)

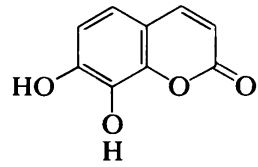


crosslinked gelatin molecules

Pyrogallol and catechol have been widely used as the developing agents in tanning developers because of their strong gelatin crosslinking action and the excellence of the image relief structure. Hydroquinone gives excessive contrast to the image unless other developing agents are present. The usefulness of even the most effective tanning developing solutions is limited by the rapid oxidation that these solutions undergo. Recently, E. F. Rul et al.[121] studied derivatives of pyrogallol and catechol as well as of benzopyrilium and coumarin in an effort to find tanning developing formulations of greater resistance to aerial oxidation.

The tanning action was found to depend very much on the nature of any substitution on the molecule of the developing agent. Introduction of electropositive methyl and methoxy groups in the catechol molecule enhanced the speed of tanning development. The introduction of electronegative groups, such as carbonyl and carboxy, produced the reverse effect. The presence of one bromine atom on the ring of pyrogallol and catechol had little effect, but increasing the number of bromide atoms in the molecule caused the tanning action to be inhibited. However, none of the substituted developing agents was superior in gelatin relief structure to that given by a pyrogallol developer itself.

The compound, 7,8-dihydroxycoumarin (daphnetin),



is a ringed derivative of pyrogallol. Alone in tanning developers, daphnetin produced relief images with unsharp edges. However, with some daphnetin derivatives combined with pyrogallol in tanning developers, fine-grained relief images were produced. In developers containing approximately equimolecular amounts of 4-methyldaphnetin and pyrogallol the useful lifetime of the solution was found to be three times longer than that of a pyrogallol developer. The developing-hardening properties of 6,7-dihydroxycoumaranone-3 and thiazolyl derivatives of catechol and pyrogallol have also been studied.[122,123]

The tanning action of a pyrogallol-daphnetin solution could be increased by the addition of Phenidone or 4-methyl Phenidone. Phenidone appeared only to increase the silver development and not to influence the tanning by the oxidation products of the pyrogallol. A formulation was compounded with these three developing agents, potassium bromide to control fog, and the combination of sodium carbonate with sodium sulfate to minimize swelling

to secure optimum relief structure. This tanning developer had the composition

Pyrogallol	3 g
4-Methyldaphnetin	4 g
Phenidone	0.05 g
Sodium carbonate, anhydrous	50 g
Sodium sulfate, anhydrous	150 g
Potassium bromide	2 g
Water to make	1 liter

According to Rul et al., "Compared to Metol-pyrogallol and Phenidone-pyrogallol developers this developer has longer life and is less sensitive to variation in processing conditions; moreover, it produces better relief microstructure with good relief wash-off." By studying the photomicrographs of the structure of matrix reliefs, Rul et al.[124] found that the average dimension of the gelatin grains of the relief depended on the optical density of the relief, the exposure, the time of development, and the nature and concentration of the tanning developing agent.

The nature of the tanning intermediates in pyrogallol tanning solutions has been studied by electron paramagnetic resonance, a method that detects the presence of the semiquinones formed during development. When the semiquinone concentration reaches its maximum concentration, two molecules join together to form the semiquinone of 3,3′,4,4′,5,5′-hexahydroxydiphenyl.[125] It was noted that "the value of the electron paramagnetic resonance signal of photographic emulsions before and after a prolonged wash remained almost unchanged. This observation confirms the correctness of the assumption that the compounds having electron paramagnetic resonance are bound with gelatin of the photographic emulsion."[126] Dimers and trimers, as well as monomers, of oxidized pyrogallol were found to crosslink the gelatin of the emulsion layer.[127] Peroxide treatment, known to form polymers of the oxidized form of the developing agent, supported the evidence that such polymers are formed.[128] Spectroscopic investigations have also supported this concept that the products of polymerization of the tanning developing agent have a hardening effect on the gelatin.[129]

Photographic Emulsions for Tanning Development

Although the composition of a tanning developing solution and the mechanism of hardening gelatin have been examined at length, it must not be

forgotten that the formation of a relief image depends greatly on the nature of the photographic emulsion layer. According to C. A. Bongard and M. I. Vinitskaya,[130] "The composition of emulsions, that is, the ratio of gelatin, silver halide, and filter dye (pigment) in emulsion, plays a decisive role." The unexposed emulsion layer of a matrix film is unhardened. The latent image in this film must be very compact, not distributed throughout the layer. To limit the penetration of the exposing light, a light-absorbing dye or pigment is included in the gelatin layer. A yellow dye is suitable for blue-light exposures and a black pigment for any color of exposing light.

The silver halide is usually a fine-grained bromide or bromoiodide emulsion of very narrow grain size distribution, similar in type to some document-copying emulsions. The narrow spread of grain sizes insures that the grains will be of comparable sensitivity and would begin to develop together at the same time. The relationship of gelatin to silver halide quantities must be carefully determined to insure sufficient tanning product from the developed silver to obtain the maximum relief image quality. Excess tanning product may diffuse away from the developing silver halide crystals to crosslink gelatin molecules. Although this distance is very small because of the short half-life of the oxidized form, degradation of the edges of the relief image may still be significant. Tull hypothesized a diffusing radius of 1.5 μ from the developing grain.

Modern photographic emulsions designed for tanning development may contain one other compound: the tanning agent itself. Pyrogallol and catechol are unstable in emulsion layers, but related compounds are suitable for use. 4-Phenylcatechol, for example, is insoluble in water and stable in the emulsion layer. This compound must be dispersed in the gelatin layer; that is, the compound is dissolved in an organic solvent and then a colloid mill used to break up the solvent into small droplets that are distributed throughout the gelatin layer. Other catechols, such as 4-phenoxycatechol, are said to be suitable as incorporated tanning agents.[131] Polyhydroxyspiro-*bis*-indanes have been proposed as tanning developing agents suitable for inclusion in the photographic emulsion.[132]

A novel tanning agent has been proposed by William E. Lee.[133] A 1-phenyl-3-pyrazolidone tanning developing agent, such as 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone or 1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone, forms an image of hardened gelatin in the exposed areas of the photographic emulsion. Washing in hot water will remove the unexposed, unhardened silver halide emulsion, leaving a relief image. During image development an aldehyde is released, instead of a quinone from the phenolic tanning agents, which hardens the gelatin imagewise. The 4-substituted-3-pyrazolidone may be incorporated in the emulsion layer or

may be included in a processing solution. Such a tanning developer had the composition

1-Phenyl-4,4-dihydroxymethyl-3-pyrazolidone	0.44 g
Ascorbic acid	2.0 g
Sodium sulfite, anhydrous	2.0 g
Sodium carbonate, anhydrous	20.0 g
Water to make	1.0 liter

After a 5-min, 25°C, development of matrix film, the film was placed in a 5% acetic acid solution to stop development and then in water at 37°C to remove the unhardened gelatin in the unexposed areas of the emulsion. The relief image in the developed areas remained firmly attached to the film support. When 1-phenyl-3-pyrazolidone was used in place of its 4-substituted derivative above, the entire emulsion layer was removed by the hot-water treatment.

CONCENTRATED DEVELOPERS

Water is the substance that is present in the greatest quantity in a developing solution. The weight or volume of water is of little consequence to the user who makes his developer from formula or from powdered preparations. The transportation of water, however, adds greatly to the shipping cost of developers prepared by photographic manufacturers. This has led to the sale of concentrated developers, which are diluted with water before use. Concentrated developers have other advantages, however, besides shipping economy. The entire amount of a premixed powder developer must be dissolved, even though only a part of the solution is needed. A fraction of the heterogeneous powder cannot be used, because it may differ in composition throughout its bulk. A small quantity of a concentrated solution is the same as the rest of the solution. A quantity of the concentrated developer can be diluted with sufficient water to provide the desired volume of a one-time-use developing solution. Most concentrated developers have excellent stability, so that they can be stored for long times before use.

The convenience and desirability of concentrated developers has long been recognized. The classic concentrated developer is Rodinal, a sodium hydroxide solution of *p*-aminophenol which is usually diluted with 20 to 100 times its volume of water. The difficultly soluble free base of *p*-aminophenol hydrochloride would be precipitated in sodium carbonate solution,

but the highly soluble *p*-aminophenolate is formed in sodium hydroxide solution. A very slight excess of the free base of *p*-aminophenol acts as a preservative for the concentrated solution. The preparation of the Rodinal-type developer was known for many years before 1920, when W. F. A. Ermen gave this preparation for the concentrated developer[134]:

Place 250 c.c. of water in a beaker and heat to the boil. Remove from the flame, add a few crystals of potassium metabisulphite, 20 grams of para-amidophenol hydrochloride, and 60 grams of potassium metabisulphite. Stir until all the bisulphite has dissolved, and then with constant stirring add commercial (70 deg. Twaddell) caustic soda liquor (a 40% sodium hydroxide solution). At first the mixture thickens, owing to the precipitation of amidophenol base, but on the addition of more caustic liquor this begins to dissolve.

The addition of caustic soda is stopped when the precipitate has nearly all disappeared, when the solution is made up to 400 c.c.s, placed in a rubber-stoppered bottle and allowed to cool. If the operation has been carried out correctly, a further crop of amidophenol will have crystallized out, and this is then nearly all dissolved by the addition of a few more drops of caustic liquor. It is very important to leave a small quantity of amidophenol undissolved, as the least excess of caustic soda causes the solution to be unstable; it rapidly turns brown even in a closed bottle, deteriorates in strength, and is liable to cause fog. A properly made solution has been used by the writer continuously for over two years, and the last drop had practically the same development energy as the newly made solution.

The quantity of 70-deg. Tw. caustic liquor required for the above quantity is about 68 to 70 c.c.s. Should the caustic have been added in excess, the matter may be remedied by the addition of a little strong bisulphite solution to the cold liquor, until a slight permanent deposit of the amidophenol forms. This may be filtered off if desired, but it does no harm, as it will all dissolve when the concentrated solution is diluted to developer strength.

For film use the concentrated developer is diluted with 15 to 30 times its volume with water, or up to 40 volumes of water for photographic bromide prints.

Metol is a substituted *p*-aminophenol and it has been used to prepare concentrated solutions. Metol has been combined with hydroquinone in the caustic solution. Edgar H. Booth has suggested this method of formulation of a MQ Rodinal-type concentrate[135]:

Metol	5.7 g
Hydroquinone	22.6 g
Distilled water	415 ml

Heat the water to 50°C (122°F) and then dissolve in it the Metol and the hydroquinone. Then add

Sodium sulfite, anhydrous	77.7 g

Stir for 2 min, producing a grayish-white precipitate. Then add

Sodium hydroxide	14.5 g

Stir until all the sodium hydroxide is dissolved and then the white precipitate will have disappeared. Filter quickly and store in small rubber-stoppered bottles. For use, the concentrate is diluted with 15 to 30 parts of water. For known overexposure, Booth recommended the addition of 5 drops of 10% potassium bromide for each 30 ml of the mixed solution of the concentrate diluted with 15 parts of water.

A liquid developer concentrate should contain the maximum concentration of the ingredients without crystallization occurring, even at low temperatures. Only limited quantities of sodium sulfite, sodium carbonate, or sodium metaborate can be dissolved in the concentrate, but the potassium salts permit more of these compounds to be present. Alcohols and glycols are often added to help solubilize the developer ingredients. Often a sequestering agent is added to prevent precipitates from forming when the concentrated solution is diluted. The compounding of concentrated developers requires a careful balancing effort to secure maximum concentration of ingredients to provide an energetic solution after dilution, yet prevent crystallization or deterioration of the concentrate until used.

As already indicated, *p*-aminophenol hydrochloride and Metol-hydroquinone are suitable as developing agents in concentrated developers. Most modern concentrates contain Phenidone rather than Metol, because Phenidone requires smaller amounts than Metol for equivalent activity and is free of toxicity. Phenidone may be used alone to make a soft-working developer of the composition[136]:

1-Phenyl-3-pyrazolidone	3 g
Sodium sulfite (crystalline)	25 g
Sodium carbonate (crystalline)	50 g
Potassium bromide	0.5 g
Water to make	500 ml

For use, one part of this solution is diluted with three parts of water.

Most developer concentrates contain two superadditive developing agents, such as Phenidone and hydroquinone, with a great degree of dilution. After dilution with hard water, however, the ready-to-use solution of developing agents and potassium salts becomes cloudy after slight use. This

tendency to form precipitates can be prevented by including a compound such as ethylenediamine tetraacetic acid in the concentrate.[137,138]

Potassium sulfite	312 g
Potassium hydroxide	15 g
Potassium carbonate	90 g
Hydroquinone	45 g
1-Phenyl-3-pyrazolidone	1.5 g
Potassium bromide	10 g
Ethylenediamine tetraacetic acid	8 g
Water to make	1 liter

Even greater freedom from cloudiness was obtained when 50 g of the ethylenediamine tetraacetic acid was present with enough potassium hydroxide added to maintain the pH at 10.7. A developing solution for photographic papers can be made by dilution of the concentrate with seven parts of water. Concentrates containing a high concentration of difficultly soluble ingredients may precipitate upon standing, especially at low temperatures. Such precipitation may be prevented, it is claimed in U. S. Pat. 3,276,875, by including from 20 to 100 g of *N*-methyl-2-pyrrolidone in the concentrate.[139]

It is essential in X-ray developers to maintain contrast throughout the replenished life of the solution. The developer concentrate may be used as a replenisher for the used solution, but the starting developing solution must be adjusted to the starting pH and bromide concentration from the higher activity of the developer concentrate. The following X-ray developer concconcentrate and starter solution has been proposed[140,141]:

Concentrated Developer Solution

Water	250 ml
Ethylenediamine tetraacetic acid	20 g
Potassium sulphite solution (650 g/liter)	580 ml
Potassium hydroxide (90% pure)* approx.	81 g
Boric acid	25 g
Hydroquinone	75 g
1-Phenyl-3-pyrazolidone	2 g
5-Methylbenzotriazole	0.3 g
1-Phenyl-5-mercaptotetrazole	0.3 g
Water to	1000 ml

* Variable to give a pH of 11.95 ± 0.05.

Starter Solution

Water, approx.	430 ml
KBr	311 g
HBr (47% w/w)	204 ml
Water to	1000 ml

Working-strength developer and replenisher solutions are then made up as follows:

Working-Strength Developer (pH 10.90 ± 0.05)

Concentrated developer	100.0 ml
Starter solution	7.7 ml
Water to	1000.0 ml

Replenisher

Concentrated developer	200.0 ml
Water	800.0 ml

This replenisher was added to the working-strength developing solution at the rate of 30 ml/sq ft of film processed.

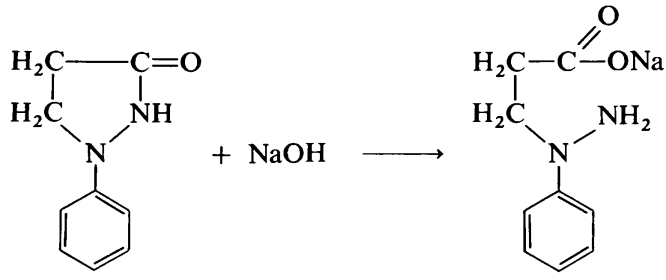
Instead of hydroquinone, another developing agent may be used with Phenidone in developer concentrates. Fine-grain images are said to result when photographic Glycin is combined with Phenidone, as in the concentrate[142]:

Potassium sulfite (71% w/v)	422 ml
p-Hydroxyphenylaminoacetic acid	40 g
1-Phenyl-3-pyrazolidone	2 g
Water to make	1 liter

This concentrate is diluted with nine parts of water, then about 13 g solid sodium hydroxide added to make the pH 9.1. Exposed, fast panchromatic film, developed 10 min at 68°F, produced a fine-grain image of high photographic speed.

In the above developing solution a concentrate of the developing agents in a strong sulfite solution is prepared, but the alkali must be added after dilution of the concentrate for use. This extra step of adding the alkali component is necessary because Phenidone has been found to be unstable when stored in liquid alkaline solutions. Although Phenidone has many desirable properties, L. F. A. Mason[143] concluded, "The biggest disadvantage

of Phenidone is its instability in alkaline solution." G. C. Alletag[144] found "Phenidone degradation apparently occurs to some extent in all alkaline Phenidone developers. The rate at which degradation takes place depends primarily on the alkalinity of the developer and on the storage temperature. The loss of activity caused by Phenidone degradation depends on the characteristics of the developer, such as the original concentration of the developing agents present and the alkali-restrainer balance." Prepared liquid alkaline developer concentrates containing Phenidone have limited storage life, presumably due to an opening of the pyrazolidone ring



1-phenyl-3-pyrazolidone | sodium hydroxide | sodium salt of phenyl hydrazine-propionic acid

This deterioration of Phenidone in alkaline solutions can be avoided by dissolving the compound in a nonaqueous organic solvent, as described in British Patent 948,294.[145,146] The concentrated developer thus consists of two solutions:

One being a concentrate of 1-phenyl-3-pyrazolidone in a non-aqueous or substantially non-aqueous organic solvent and the other being an aqueous solution containing the other ingredients normally present in a 1-phenyl-3-pyrazolidone-containing developer solution. When used as a concentrate, it is desired to keep to a minimum the volume of the second, aqueous, solution which also normally has a pH value of 9.5 or above. Addition of the 1-phenyl-3-pyrazolidone-containing solution to the second aqueous, highly alkaline, concentrate results in the precipitation of finely divided solid 1-phenyl-3-pyrazolidone which is difficult to redissolve and if allowed to remain in solid condition in the solution prevents the satisfactory development of photographic emulsions. In order to overcome this problem it is necessary either to dilute the second concentrate with further quantities of water before the first 1-phenyl-3-pyrazolidone-containing concentrate is added or to add further quantities of water to the two solutions immediately after they are mixed.

These disadvantages, pointed out in British Patent 1,154,365,[147,148] may be avoided by the use of a suitable concentrate containing the 1-phenyl-3-pyrazolidone. A two-component concentrate may be prepared as follows:

First Concentrate

1-Phenyl-3-pyrazolidone	5 g
Lactic acid	15 ml
Butyrolactone to make	50 ml

Second Concentrate

Sodium metabisulfite	680 g
Potassium hydroxide	553 g
Benzotriazole	5.5 g
N-Hydroxyethyl-ethylenediamine-*N*,*N*′,*N*′-triacetic acid trisodium salt	15 g
Borax	172 g
Hydroquinone	222 g
Potassium bromide	132 g
Water to make	1 gallon

Portions, or the whole, of these two solutions may be mixed together to give a developer concentrate which is diluted one part of developer concentrate to four parts of water. The working-strength developer has a pH of 10.6.

Other acids such as formic acid, may be used for the Phenidone solution of a two-component package photographic developer.[149] Glacial acetic acid has been proposed for this purpose, as in the following formulation[150]:

Part A

Sodium carbonate	150 g
Sodium sulfite	150 g
Potassium bromide	25 g
Hydroquinone	50 g
Benzotriazole	0.2 g
Sodium hydroxide	25 g
Water to make	1 liter

Part B

Glacial acetic acid	95 ml
Water	5 ml
1-Phenyl-3-pyrazolidone	20 g

One liter of part A and 25 ml of part B are mixed together and the solution diluted to four liters to make the working developing solution.

Although the use of two-component liquid concentrates avoids loss of activity because of the degradation of Phenidone that occurs in single alkaline concentrates, it would be much more desirable to have a single liquid for dilution with water. A stable, single-solution developer concentrate, using lactic acid or boric acid as a buffering agent, has been claimed to be much more stable than previous single-solution Phenidone concentrates.[151] This stable, single-solution concentrate contained

Trisodium salt of *N*-hydroxyethyl-ethylenediamine triacetic acid (34% w/w aqueous solution)	20 ml
Potassium sulfite	400 g
Chlorohydroquinone	51 g
Hydroquinone	51 g
1-Phenyl-3-pyrazolidone	2.44 g
Benzotriazole	3.45 g
Potassium hydroxide	94.5 g
Lactic acid	23.3 g
Water to make	1.0 liter

Dilute one part of this developer concentrate with nine parts water to form working developing solution of pH 11.3.

Another approach to stable, single-solution developer concentrates has been to avoid the use of Phenidone itself but to seek more stable 3-pyrazolidones. The 4-substituted and the 4,4-disubstituted 1-phenyl-3-pyrazolidones are more stable upon storage in alkaline solution than Phenidone itself.[152] Connecting the 4 and 5 positions of the 3-pyrazolidone ring to form a five-membered or six-membered ring has been claimed to produce "substantially higher resistance to hydrolysis on keeping."[153] The introduction of groups on the 4 and 5 carbons of the 3-pyrazolidone ring does decrease the degradation of the developing agent in alkaline solution, but the substituted compounds may have even lower water solubility than the difficultly soluble Phenidone. The substitution of a hydroxymethyl or morpholinomethyl group on the 2 carbon is said to improve the solubility of the modified Phenidones without decreasing photographic developing activity.[154]

Another approach to stable developer concentrates has been to replace the 3-pyrazolidone with a 3-aminopyrazoline which, in the presence of

hydroquinone, has "an excellent resistance to oxidation and to hydrolysis."[155] An example of such a concentrate included

Potassium carbonate	200 g
Potassium sulfite	200 g
Potassium hydroxide	30 g
Hydroquinone	30 g
1-*p*-Aminophenyl-3-aminopyrazoline hydrochloride	1.5 g
Diethylene glycol	100 g
Potassium bromide	15 g
Water to make	1 liter

For use the concentrate is diluted with water in the ratio of one part of concentrate and seven parts of water. The photographic activity of the concentrate was said to remain unchanged even after the concentrated solution, sealed in a glass bottle, had been stored at 60°C for 12 weeks.

In order to reduce their bulk, developer concentrates have been prepared in the form of viscous liquids, pastes, and tablets.[156] Richard W. Henn[157] proposed "a concentrated developer in which the solid developer constituents are held in a uniform suspension in a colloid comprising alginic acid, salts of alginic acid or esters of alginic acid from which they will dissolve rapidly to form the developing solution." The developer constituents were first ground to pass through an 80-mesh screen before being added in succession to 90 ml of a 2% solution of Kelgin, which is a sodium derivative of algin having medium viscosity.*

Sodium sulfite	24.0 g
Sodium carbonate	45.0 g
Monomethyl-*p*-aminophenol sulfate	1.6 g
Hydroquinone	4.8 g
Potassium bromide	1.0 g
Sodium tetraphosphate	2.0 g

A stiff, smooth gel of slightly over 100 ml is produced. One part of gel dissolved in 16 parts of water is a suitable developing solution for photographic

* Available from Kelco Co., San Diego, Calif.

prints; diluting one part of gel to 32 parts of water produced a developer for photographic negatives.

One difficulty in compounding a developer concentrate is getting sufficient inorganic salts into the concentrated solution and then keeping them from precipitating, especially at low temperatures. One way to avoid this problem is to use liquid organic amines and liquid organic amine–sulfur dioxide addition products to which only the developing agents need be added.[158] Because they contain very little or no inorganic salts, such as those commonly found in most developing solutions, these concentrates can be prepared so that high dilutions with water are possible. The organic amine serves as an organic activator for the developing agents, and the organic amine-sulfur dioxide addition product provides sulfite ions for the developing-solution preservative.

As pointed out in U. S. Patent 3,552,969,[159,160] "The solvent action for silver halides of organic amines typically employed as the activators has given rise to silver stains, i.e., dichroic stain, on certain photographic elements developed with these compositions. Such stains which appear on the surface of processed photographic elements, especially photographic film, are apparent as a deposit of fine or colloidal silver. This problem has been troublesome especially with fine grain silver halide films." Known antistain compounds, such as 2,4-dihydroxybenzophenone or chlororesorcinol, or *N*-methylpyrrolidone, were not effective in counteracting the formation of the silver stain, but polyvinylpyrrolidone was effective in the organic amine developer concentrates. A liquid developer concentrate with this compound had the following components:

2,2′-Iminodiethanol-sulfur dioxide addition product	31.0 g
2,2′-Iminodiethanol	9.0 g
2,2′-Iminodiethanol hydrobromide	1.5 g
1-Phenyl-3-pyrazolidone	0.5 g
Hydroquinone	6.0 g
2-Aminoethanol	5.0 g
Ethylene glycol	10.0 g

In each liter of this mixture is dissolved 0.25 g polyvinylpyrrolidone, such as PVP Grade K-15, a product of GAF Corp. One part of this mixture was diluted with 31 parts of water to form the developing solution for a medium-grain silver bromoiodide film. Development for 8 min at 21°C produced a film free from dichroic stain without loss of film emulsion speed.

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Chapter 12
Stop Baths

To many workers, the stop bath is merely a splash of acid in a vague amount of water. It should be compounded as directed.

ANSEL ADAMS[18]

Development is rarely carried to completion, resulting in the actual use of only a small portion of the silver halide. The photographic film or paper is removed from the developer at a time when sufficient metallic image has been formed. Image formation still continues, however, as the gelatin emulsion layer has imbibed a considerable quantity of the alkaline developer. The activity of this absorbed developer may be diminished by diluting the imbibed developer with water. Rinsing in water is satisfactory with the weakly alkaline, slower-acting developers, but uneven image formation may result when the developer is a rapid-acting, highly alkaline solution. With vigorous developing solutions an acid bath is used immediately following the development. The acid of this bath, called a shortstop or stop bath, neutralizes the alkali of the developing solution, thus inactivating the reducing action of most developing agents.

The stop bath is the first step in a series of postdevelopment treatments that are essential to preserve a permanent photographic image. After the developing action has been stopped, the undeveloped but still light-sensitive silver salts of the emulsion must be removed, or these salts will color and obscure the image detail. The silver halides of the emulsion have extremely

low water solubility, so that washing in water would be ineffective. In practice, we make these silver halides water soluble by reacting them with the fixing agent contained in the next photographic solution—the fixing bath. The fixing agent combines with the unused silver ions in the emulsion to form a water-soluble complex ion. This complex is removed by washing with water, the third essential step after development. The processing of the film is then completed by drying the thoroughly washed film or paper under dust-free ambient conditions or by using filtered heated air. The gelatin surface of photographic prints is sometimes dried in contact with a smooth metallic surface to produce a glossy-surfaced print.

A careful control is required of the entire postdevelopment treatment of stop-fix-wash-dry cycle if a high-quality permanent image is to be obtained. The stop bath must be of a composition that will not be detrimental to the fixing bath, as some of the stop bath will be carried over into the fixing bath. The ingredients of the fixing bath as well as the silver complexes must be readily removed from the gelatin layer to prevent future attack upon the silver image. It is essential that the gelatin of the emulsion layer must not swell with liquid to the point of rupture. To prevent this, gelatin hardening agents are often added to the stop or fixing bath. Sodium sulfate may be present in a stop bath to prevent excessive swelling of the gelatin emulsion layer. Thus, though sometimes neglected in the concern for development, the postdevelopment steps are vital for maintaining and preserving the developed silver image.

STOP BATHS

When a photographic material is removed from the developer, the emulsion layer, swollen by the alkaline developing solution, contains the chemical constituents of the developer, the chemical components of the emulsion, such as silver halide, chemical and spectral sensitizers, and antifoggants, and the reaction products of these two interacting systems. Image formation will continue even though the film or paper is no longer immersed in the developer, often resulting in image mottle or streakiness. The danger of image nonuniformity may be minimized by a thorough and rapid draining immediately after removal from the developer so that the continuing development will proceed as uniformly as possible until stopped. A suitable wetting agent in the developer has been used to insure more rapid draining.

Image formation may be brought slowly to a stop by immersing the photographic material in water. Water stop baths of 30 to 60 sec duration have often been recommended, especially following a fine-grain or high-definition developer of low alkalinity. In this case the water bath acts as the

second bath of a two-bath developer. However, image nonuniformity may result from the use of a water stop bath following development in a highly energetic buffered developer of high pH. An acidic stop bath is required in this case because development is stopped more quickly by the neutralization of alkali of the remaining developer, inactivating the developing agents. Acid stop baths are necessary to prevent aerial fog during machine processing when the photographic material must be exposed to the air during transfer from one processing solution to the next.

With either the water rinse or the acid stop bath, image development does not stop the instant the photographic material is immersed in the bath. Cessation of image formation begins at the top of the gelatin layer and proceeds through each level of the emulsion until the base is reached. Developer diluted with water or the salts of the acid-base neutralization may be formed as the stop bath diffuses deeper and deeper into the emulsion layer. Agitation is needed to remove these spent solutions so that they may be replaced with fresh stop bath. Even moderate agitation can reduce the neutralization time by one half, thus helping to produce more uniform images.

According to R. W. Henn and J. I. Crabtree,[1] "The speed of neutralization is dependent on (a) the nature and thickness of the emulsion, (b) the degree of acidity or pH, (c) the total acidity, and (d) the degree of turbulence. These factors have been studied by immersing films or paper in a developer, Kodak Dektol developer, containing an indicator dye like phenolphthalein, and then transferring them to the Kodak SB-5 stop bath and noting the time required to neutralize the absorbed developer and dye." These writers add that the more acid the bath, the more rapid is the neutralization, but the total acidity of the solution must also be considered. "Total acidity," Henn and Crabtree have pointed out, "differs from the *degree* of acidity or pH value in being a function of the reserve acidity, and in a buffered system, widely different quantities of reserve acidity may be present at the same pH value. An analogy may perhaps be reached by comparing two cars of widely differing horsepower which are moving at the same rate along a level road; when they reach a steep hill, the greater reserve power of the car with the higher horsepower will be noted."

The greater the thickness of the emulsion layer, the longer the time for the acid stop bath to penetrate and neutralize the alkaline developing solution in the layer. For a given photographic material, the pH and total acidity of the stop bath, and the agitation during the neutralization, are the primary factors involved. The effects of these factors were demonstrated by Henn and Crabtree using their dyed film technique, the results being shown in Figure 1.

Figure 1(*a*) shows the effect of the degree of acidity upon the neutralization time. Dyed film is immersed in a 1.3% solution of acetic acid adjusted to the pH level indicated, then the time to penetrate (neutralize) is noted.

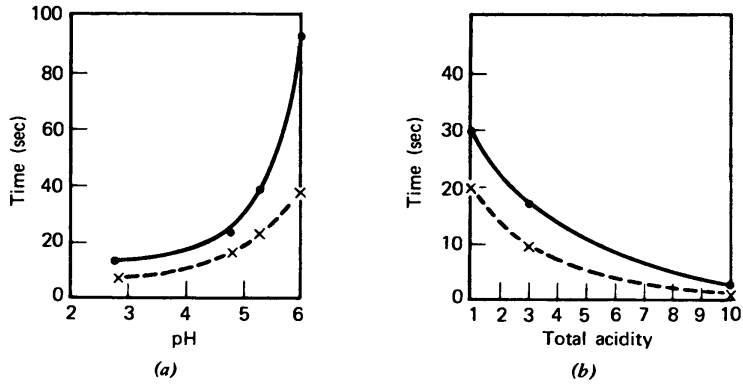

Figure 1. Effects of (*a*) degree of acidity and (*b*) total acidity on neutralization time. [R. W. Henn and J. I. Crabtree, PSA J., 17B: 14 (1951).]

The solid curve indicates that the more acid the solution, the more rapid the neutralization. The dotted curve shows the great effect of agitation in decreasing the neutralization time.

Figure 1(*b*) shows the effect of total acidity upon neutralization time. The pH of the acetic acid solution has been maintained at 4.8, but the total acidity has been varied by adding increasing amounts of acetic acid and sodium acetate. The solid curve shows that the higher the total acidity, the more rapid is the neutralization. The dotted line shows the great influence of agitation.

Sometimes, during machine processing, the development is allowed to continue in the stop bath under carefully controlled conditions. Desirable edge effects may be formed that enhance image sharpness. In most cases, however, an acid stop bath is used to (1) stop image formation as quickly as possible, (2) make the emulsion layer acid so that it will be more compatible with the acid fixing bath, and (3) remove calcium scums, usually calcium sulfite, or aluminum deposits, such as aluminum phosphate, that formed on the surface of the emulsion during development.

The acid stop bath, sometimes with a gelatin hardener in the solution, will be imbibed in the emulsion layer and carried into the fixing bath. The acid content of the stop bath must be compatible with the fixing bath. If the bath is not sufficiently acid, development may not be stopped, resulting in streaked images. Image formation will continue to occur when the film is still in the fixing bath. The fixing agent will begin to dissolve the silver halide, taking the silver ions into solution. However, the still-active developing agents can react with this solubilized silver, precipitating it as a metallic film on the

surface of the emulsion. This surface deposition is called dichroic (two-color) fog because it appears yellow-green when viewed by reflected light and pinkish-purple when viewed by transmitted light. The presence of active developer in the fixing bath may also result in a yellowish-brown staining of the emulsion layer because of developer oxidation products.

Carryover of the unneutralized developing solution into the fixing bath will cause a gradual rise in the pH of the bath. The pH of an acid hardening fixing bath must not be allowed to rise much above 5, as the hardening agent will lose its effectiveness at higher pH values. Loss of hardening by the fixing bath will allow the swollen emulsion layer to be damaged easily by abrasion, reticulate because of excessive irreversible swelling, or frill (the gelatin layer pulls away from the base, especially at the edges of the photographic material, to form a wavy layer). (See Figure 2.) If the alkalinity of the fixing bath is allowed to rise because of the alkaline developing solution being carried into it, some of the hardener may sludge from solution, causing a tenacious surface scum to form on the emulsion layer. Fixing baths based on ammonium thiosulfate as the silver halide solvent must be kept below about pH 5 or ammonia may be liberated by the developer alkali, producing dichroic fog or stains on the photographic material.

The nature of the acid hardening fixing bath fixes the upper limit of pH between 5.0 and 5.5 for the acid stop bath that must come before the fixing bath. The lower pH limit of the stop bath is determined by the nature of the developing solution as well as the limitations of the fixing bath. Developers contain sodium sulfite that will be transferred into the acid stop bath. At a pH much below 4 the acid of the stop bath will liberate sulfur dioxide from the sulfite. Sulfur dioxide is a very pungent and disagreeable gas with a sulfurous odor. At pH values of 3 or less, blistering of the emulsion layer may result because of the rapid liberation of sulfur dioxide or other gases, such as carbon dioxide from the carbonate of the developing solution.

An emulsion layer still containing developing solution may swell to a dangerous extent when immersed in a strong acid bath of low salt content. This adverse effect may be counteracted by the presence of about 5% sodium sulfate in the stop bath. Effective stop baths containing sodium sulfate may be made with a pH of 3, but highly acid emulsion layers require longer to fix than when the layers of a less-acid pH enter the fixing bath. Stop baths of lower acidity than a pH of 3, although very effective in stopping development quickly, may cause the precipitation of sulfur from the thiosulfate of the fixing bath. This sulfur is precipitated in the gelatin layer and is very difficult to remove during the washing step. Thus, to be effective and compatible with the other photographic solutions, the stop bath should maintain its acidity between pH limits of 3 and 5.5. "The neutralization time was doubled as the pH was raised from 3 to 5 and became very long at a pH of 6. It is obvious,

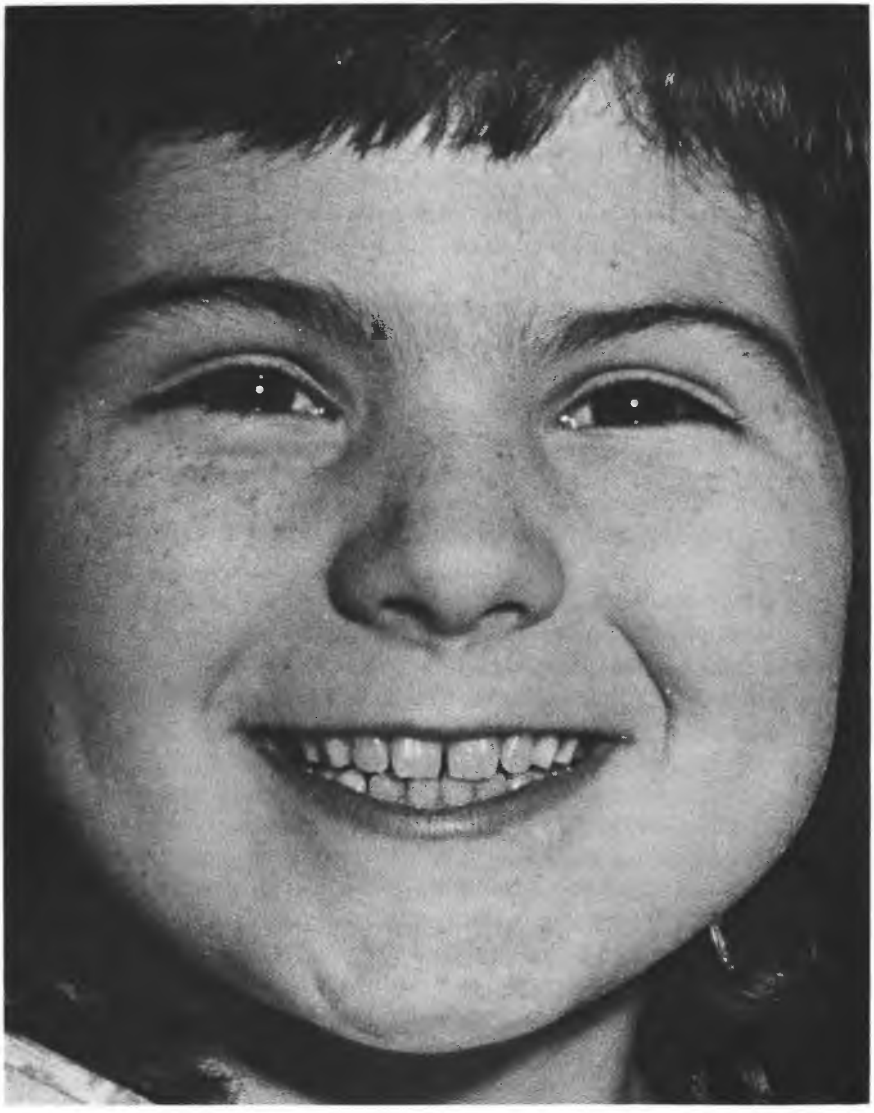

Figure 2. Reticulation is the result of excessive irreversible swelling of the gelatin of the emulsion layer. The fine ruptures can occur during the water rinse or in the stop bath of low salt content following development in an alkaline developer. (Photograph by Grant Haist)

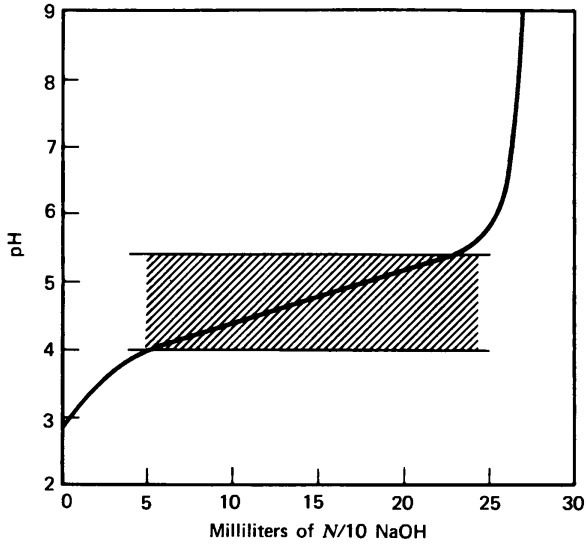

Figure 3. The neutralization curve of acetic acid with sodium hydroxide shows a buffer range (shaded area) where a considerable amount of hydroxide may be added without causing a great change in the pH of the solution. Data are for 25 ml of 0.6% acetic acid neutralized by 0.1 normal sodium hydroxide. [R. W. Henn and J. I. Crabtree, *Phot. Sci. and Tech., PSA J.*, 17B (4): 14 (1953)]

therefore, that an acid stop bath is useless long before it is completely neutralized at a pH of 7."[1]

Total acidity is a measure of the reserve acidity that is available to buffer changes in pH. Ideally, for an acid stop bath, an acidic substance is needed that will react with the alkali of the developer without any rapid change in pH. With acetic acid–sodium acetate solutions the alkali neutralization time decreased rapidly with the increase in total acidity (acetate content). The time for neutralization for a 10% acetate solution was only about one-tenth that of a 1% solution. In the neutralization of acetic acid, about one-fifth of the total acidity lies below pH 4, about one-fifth above pH 5, and the remaining three-fifths between the pH's of 4 and 5. Thus four-fifths or 80% of the total acidity of an acetic acid bath would be neutralized when the bath reached a pH of 5. (See Figure 3.) It is essential that sufficient reserve acidity be present in a used stop bath, as each roll of film (80 sq in.) carries about 10 to 12 ml of developer into the stop bath. This volume of developer is absorbed in the gelatin layer and on its surface.

Because of the necessity of maintaining a stop bath below pH 5, an indicator dye may sometimes be added to the bath to give a visual indication of the bath's acidity. A few drops of a 0.5% alcoholic solution of bromcresol

green is a suitable indicator for film stop baths. The indicator dye may be impregnated in a paper strip, which is dipped in the stop bath solution. At pH 4.5 to 5 the indicator dye will be green, becoming blue as the pH rises. Below pH 4 the dye will be yellow. Thus, when the dye becomes blue, the stop bath should be discarded or acetic acid added until a yellow-green color is achieved.

For adding the indicator dye permanently in the stop bath, 3-alizarin-sulfonic acid, sodium salt, has been recommended. This dye is yellow in acid solution, changing to pink with low acidity, and finally to violet with an alkaline solution. A suitable formula for the dye solution is

Water	300 ml
1-Methoxy-2-propanol	200 ml
Sodium 3-alizarinsulfonate	5 g

The number of drops of this solution to be added to the stop bath solution must be determined for the desired working conditions. "To do this," according to Carlos Julio Risso-Dominguez,[2] who suggested the above formulation, "the tray where the stop bath is used should be filled with water rendered weakly alkaline with a small amount of sodium carbonate and, reproducing the same conditions, the necessary drops should be added until a darkening of the solution is noted. This should be done with some agitation in order to insure that the dye is thoroughly diffused in all the bath."

Stop baths may be maintained with less pH variation by adding about 1 ml of glacial acetic acid for each 80-sq-in. roll of film. Replenished stop bath should be discarded when the volume of the added acid equals the original volume of the bath; this procedure minimizes staining problems due to the ingredients of the developer that contaminate the stop bath with use. The Kodak SB-5a stop bath formula is suitable for film if replenishment is planned.

Kodak SB-5a Stop Bath

Acetic acid, 28%	64 ml
Sodium sulfate (desiccated)	45 g
Water to	1000 ml

A simple stop bath may consist of 30 ml of glacial acetic acid in a liter of water.[3] Most published photographic formulas list the use of 28% acetic acid rather than the readily available glacial acetic acid (99.5 to 99.7% acetic acid). Lloyd Varden[4] has pointed out that glacial acetic acid is a strong acid,

irritating to the skin and eyes, whose poisonous nature is best avoided under most darkroom conditions. For these reasons, most photographic manufacturers recommend the use of 28% acetic acid for making stop baths and also for making fixing baths where the glacial acetic acid may decompose some of the ingredients, such as the sodium sulfite. If glacial acetic acid is assumed to be 100% acetic acid (a small error), then 28 ml of the glacial acetic acid in 100 ml of aqueous solution would make the specified 28% acetic acid. A chart has been prepared by F. M. Brown[5] to aid in the preparation of 28% acetic acid from glacial acetic acid (99.5% acid). To use this chart (Figure 4), find on the horizontal line the volume of 28% acetic acid needed. Measure up from this point until the diagonal line is reached, then horizontally to the left to read off the amount of glacial acetic acid that must be added to sufficient water to make the desired volume of 28% acetic acid.

Many acids may be used in stop baths, but compatibility of the acid with the fixing bath must be a determining factor. A considerable volume of the stop bath will be carried over to dilute the fixing bath, so it is important that the acid should have properties similar to or compatible with those of the acid present in the fixing bath. Solid organic acids, such as citric, diglycolic, tartaric, maleic, malic, or oxalic, may be suitable to stop development in the stop bath, but if carried into the fixing bath, these acids may form complexes with the metal ions of the hardening agents, thus weakening the hardening properties of the fixing bath. Acid salts, such as sodium bisulfite and potassium metabisulfite, are effective acidic compounds that do not interfere with

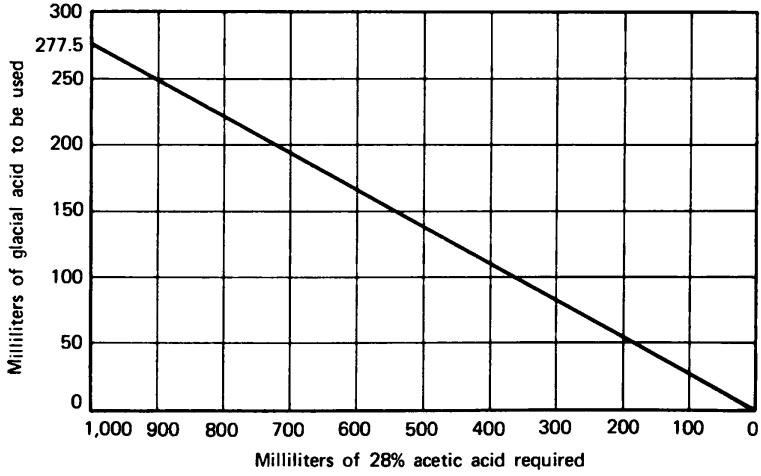

Figure 4. Chart to aid in preparing 28% acetic acid from glacial acetic acid. [F. M. Brown, *Photo Technique*, 2 (9): 76 (1940)]

the hardener of the fixing bath. A 5% solution of potassium metabisulfite gives off considerable sulfur dioxide which would be objectionable in a small darkroom. However, acetic acid is used universally as the acidic substance in stop baths because this acid is economical, readily available, and does not precipitate sulfur or interfere with the hardening of the fixing bath.[6] Acetic acid is commonly used as the acid in the fixing bath, too.

Because of the desire to shorten the time of the processing cycle of photographic materials, developing solutions of high activity (high alkalinity) are sometimes used with photo materials that are highly hardened during manufacture. Even 3 to 5% acetic acid stop baths may not be sufficient to stop development in time to prevent unwanted image formation. The alkali of the developer reacts with the acetic acid to form sodium acetate. The presence of this compound reduces the ionization of the acetic acid so that the pH may rise to a value above 2.5, the pH of a 3% acetic acid solution.

Dilute solutions of stronger acids, such as hydrochloric, phosphoric, or sulfuric, may have to be used. A 2% sulfuric acid solution has a pH of about 1.0. Quick-acting sulfuric acid stop baths neutralize the developer alkali, forming highly ionized sodium sulfate that does not materially change the low pH of the bath. The transporting and measuring of sulfuric acid is a potential hazard, so the salt, sodium bisulfate monohydrate, has been suggested as a source of sulfuric acid.[7] Fifty-seven grams of this compound in a liter of water (49.5 g of the anhydrous salt) was found to be equivalent to a 2% sulfuric acid solution, although the pH of the bath made from the salt is not quite as low as when the acid is used.

A patented stop bath concentrate has the following composition:

Water	325 ml
Sulfuric acid (concentrated, 95 to 96%)	220 ml
Ammonium sulfate	526.9 g
Sodium bisulfate monohydrate	308 g
Water to make	1000 ml

If available, a stoichiometric amount of ammonium bisulfate may be substituted for the sulfuric acid and the ammonium sulfate, but ammonium bisulfate is a relatively uncommon compound. For use, one part of the above concentrate is diluted with 10 parts of water, giving a working solution with a sulfuric acid equivalent concentration of about 4% by weight.

The use of sulfuric acid stop baths may result in serious corrosion of metal tanks, even those made of Type 304 or Type 316 stainless steel. When sulfite ions are carried into a sulfuric acid stop bath in a steel tank, ferrous sulfide and hydrogen sulfide gas are produced. Some of the metal of the tank is used

in the reaction, eventually causing the tank to be eaten away. Titanium or plastic materials are resistant to corrosion from sulfuric acid stop baths. Special stainless steels also may be found suitable.

Boron compounds have been found to be beneficial in both developing and fixing solutions. In an alum fixing bath, for example, certain boron compounds broaden the pH range over which the gelatin hardening by alum is effective and raise the pH value before a precipitate forms, thus extending the useful life of the fixing bath. If compounds such as boric acid, borax, boron triacetate, glycol borate, phenyl borate, or the glyceryl esters of boric acid are added to the stop bath, then boron compounds need not be present in the fixing bath. In a U.S. Patent Harold D. Russell[8] claimed stop baths consisting of compounds yielding a borate ion and an organic acid, such as acetic acid, propionic acid, or butyric acid. Formulations for suitable boron-containing stop baths included 3% boric acid (30 g boric acid in sufficient water to make one liter) or

Borax	50 g
Glacial acetic acid	20 ml
Water to make	1 liter

Lithographic printing plates can be made by processing a silver halide emulsion layer in a tanning developer to form an image that contains areas that will accept printing ink and other areas, wetted with water, that repel the ink. In practice, the wetted areas may accept traces of ink, thus decreasing the quality of the printed image. This defect can be minimized by treating the image, after development, in a stop bath "compounded by mixing an aqueous solution of a norbornylene glycol and an acid or acid-salt, for example, phosphoric acid, a dihydrogen phosphate, acetic acid, glycolic acid or citric acid."[9] The stop bath should have a pH between 2 and 4.5, may contain a salt of the acid for improved buffering, and may include an organic solvent for the glycol, such as ethyl alcohol or 2-ethoxyethanol. An example for a concentrated solution contained 24% by weight of a norbornylene glycol and 13.2% by weight of phosphoric acid (85% strength). This concentrate may require up to eight times dilution to make the working solution of the stop bath.

Although stop baths for specialized purposes may have a variety of ingredients, most stop baths for films or papers are based on acetic acid. The Du Pont 1-S acid stop bath contains 48 ml of 28% acetic acid and one liter of water; the Ansco 210 acid stop bath consists of 45 ml of 28% acetic acid with enough water to make one liter of solution; the Gevaert G 351 stop bath for papers has a formula of 50 ml of 28% acetic acid with sufficient

water to make one liter of solution. The Agfa 200 stop bath for papers consists of 20 ml of glacial acetic acid with water to make one liter. The Agfa 201 stop bath for films uses 40 g potassium metabisulfite with enough water to make one liter; the Gevaert G 352 stop bath for papers is made by adding 50 g potassium metabisulfite with water to make one liter of the stop bath solution.

SUBSTITUTE STOP BATHS

A shortage of acetic acid sometimes occurs during times of calamity or war, or because of a failure to maintain an adequate supply. This acid is so universally recommended by all manufacturers that substitute formulations may not be available. J. I. Crabtree, L. E. Muehler, and H. D. Russell[10] found that "a variety of acidic compounds may be substituted for the acetic acid usually employed, namely, a mixture of sodium acid sulfate or sulfuric acid and sodium acetate, citric acid, sodium bisulfite or potassium metabisulfite, and white vinegar." These investigators prepared almost identical substitute baths for three acetic acid stop baths: Kodak SB-1 stop bath for paper processing, Kodak SB-1a stop bath for film processing, and the Kodak SB-5 stop bath used for the nonswelling processing of film.

The SB-1 stop bath may be replaced by SB-6, SB-7, or SB-8 stop baths whose formulas are listed. The SB-8 bath is an almost identical substitute for SB-1. The SB-7 citric acid bath may impair gelatin hardening if considerable amounts are carried over into the fixing bath.

Kodak SB-1 Stop Bath

Water	1 liter
Acetic acid (28%)	48 ml

Kodak SB-6 Stop Bath

Water	1 liter
Sodium bisulfite	30 g

Kodak SB-7 Stop Bath

Citric acid	15 g
Water to make	1 liter

Kodak SB-8 Stop Bath

Water	500 ml
Sodium acetate (desiccated)	20 g
Sodium acid sulfate	40 g
Water to make	1 liter

If sodium acid sulfate is not available for making the SB-8 bath, 175 ml of 5% sulfuric acid may be used. To make 5% sulfuric acid add one part by volume of concentrated sulfuric acid *slowly* to 19 parts by volume of cold water and mix carefully with stirring.

The SB-1a stop bath, a stronger acetic acid version of the SB-1 bath, is suitable for stopping development by more energetic developing solutions such as those containing sodium hydroxide or Kodalk (sodium metaborate). This bath should not be used after sodium carbonate developers in order to avoid blistering of the gelatin of the emulsion layer. To increase the exhaustion life of the fixing bath, the SB-1a stop bath should be followed by a short water rinse to reduce the acid carryover. The SB-1a stop bath may be replaced by SB-6a, SB-7a and SB-8a substitute formulations.

Kodak SB-1a Stop Bath

Water	1 liter
Acetic acid (28%)	128 ml

Kodak SB-6a Stop Bath

Sodium bisulfite	75 g
Water to make	1 liter

Kodak SB-7a Stop Bath

Citric acid	37.5 g
Water to make	1 liter

Kodak SB-8a Stop Bath

Water	500 ml
Sodium acetate (desiccated)	50 g
Sodium acid sulfate	100 g
Water to make	1 liter

The sodium acid sulfate of the SB-8a formula may be replaced by adding 440 ml of 5% sulfuric acid. The 5% sulfuric acid may be made by adding one part by volume of concentrated sulfuric acid *slowly* to 19 parts of cold water by volume and mixing carefully with stirring.

Kodak SB-5 stop bath is a nonswelling acid formulation containing 32 ml acetic acid (28%) and 45 g sodium sulfate (desiccated) in a liter of water. A substitute for the SB-5 bath can be made by adding 45 g sodium sulfate (desiccated) to any of the substitute stop bath formulas. Desiccated sodium sulfate dissolves with some difficulty, tending to cake, so this chemical must be added slowly while the solution is being stirred.

White vinegar is a dilute solution of from 3 to 15% acetic acid content. The white vinegar sold in grocery stores is usually about 4.5 to 5% acetic acid. By diluting one part by volume of white vinegar with two parts by volume of water, a substitute bath may be made for the SB-1 stop bath. For the more concentrated SB-1a stop bath, full-strength white vinegar should be used. Brown vinegar may replace the white vinegar, but its strong odor and foaming tendency make it less desirable than the white vinegar.

STOP BATHS FOR INTERRUPTED DEVELOPMENT OR DEFERRED FIXATION

Lithographic films are often developed by visual inspection to select the proper moment to stop development to obtain maximum image quality. Aerial cine films are also inspected during development to insure correct development because only one exposure of the scene taken is available. A stop bath for temporarily halting development during the inspection period was proposed by Vere Maffet and Earl Delzon in U. S. Patent 3,284,199 (1966). The bath consisted of a buffer solution at a pH below that at which the developing agent or agents are active. Typical fine-grain, general-purpose, lithographic, or X-ray developing solutions have pH values in the range of 8.5 to 10.5. Such developers would be inactive below pH 8.0. One suggested buffered stop bath consisted of 6.80 g potassium dihydrogen phosphate dissolved in 900 ml water. Sodium hydroxide was added until the pH was 7.20, then the solution made up to 1000 ml with water. Another bath consisted of 80 g boric acid crystals dissolved in 900 ml water, adjusted to pH 7.20 with sodium hydroxide, and then made to 1000 ml with water. After development was in progress, the film was immersed for 20 sec in the buffered stop bath, inspected for 60 sec on a safelight table, then returned to the developer, if necessary. Density growth during the inspection period was halted, and the introduction of the buffer into the developer had minimal effect.

Under difficult traveling conditions, sufficient water of satisfactory quality may not be available to wash after fixation. In these cases the developed image may be treated in an acid stop bath, then rinsed briefly in water. L. P. Clerc[11] suggested a 5-min treatment in a bath of a volatile acid, such as 2% acetic acid or a weak acid such as 5% boric acid, followed by a short rinse in clean water. The photographic negatives are then dried, and fixation and washing are deferred to a later time when sufficient water is available.

The develop-and-stop technique has been used in modern processing to obtain rapid access to the recorded image. "Arrested development" was the name given by John R. Mertz[12] to the develop-and-stop treatment needed to view recorded images from an airborne rapid processing system. According to Mertz, "The 'arrested development' processed film can remain in the unfixed state for over a year with no deterioration of film quality, and may be fixed and washed at any convenient time, producing an archival transparency."

HARDENING STOP BATHS

The emulsion layer of a photographic film swells in an alkaline developing solution, but the swelling is limited by the salt content of the solution. When this film is then immersed in a stop bath consisting only of a water solution of an acid, the emulsion layer may continue to swell because of the acidity of the bath and the lack of restraint given by the low salt content. Gelatin hardening agents and neutral salts such as the sodium sulfate in the SB-5a formula are often added to limit the emulsion swelling in the stop bath, especially if the film processing is to be carried out at higher-than-normal temperatures. Both of these agents do lengthen the time of processing. Hardening in one solution (the stop bath) and fixing in another (in a nonhardening fixing bath) requires a greater time than the use of a simple acid stop bath followed by simultaneous hardening-and-fixing in an acid-hardening fixing bath.

Two alums, potassium chromium sulfate or chrome alum,

$$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O,$$

and potassium aluminum sulfate or potassium alum,

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 8H_2O,$$

are the double salts commonly used for hardening gelatin in acidic solutions. Chrome alum was probably the first hardening agent used for stop baths, because it was recognized early as an agent to tan gelatin, making it insoluble even in boiling water. Although they are efficient gelatin hardeners, chrome alum stop baths have serious deficiencies: (1) the hardening action may be lost even if the bath is not used, (2) when the pH of the bath has been raised

by excess alkaline developer, chrome alum stop baths precipitate a scum or sludge that adheres very strongly to the surface of the film, and (3) chrome alum baths at high temperature may stain gelatin green, although no staining is evident at regular processing temperatures if high concentrations of chrome alum are avoided. Hardening stop baths containing potassium aluminum alum are often preferred for normal temperature processing, but the acidity of these baths must also be carefully controlled or a sludge of aluminum hydroxide may be precipitated.[13]

At normal temperatures of processing, the extent of chrome alum hardening is not needed, but this compound may be useful for processing at higher temperatures or for limiting the absorption of water by the emulsion layer so that rapid drying is possible. Gelatin hardening occurs more rapidly in a stop bath than in a fixing bath, so the swelling of the emulsion layer is inhibited before it occurs.

It was found by Crabtree and Russell[14] that:

1. plain chrome alum solutions are more suitable for hardening motion picture film than those containing acid;
2. the addition of developer decreases the acidity and the hardening properties;
3. the acidity or pH value of a chrome alum solution must be maintained at a value of 4.0 for neutral film rinsed in water for 15 minutes after development and between 3.8 and 3.0 for alkaline film if the maximum degree of hardening is to be obtained; the hardening properties are constant, irrespective of the concentration of chrome alum above 0.5 per cent when the pH is adjusted to these values;
4. sulfuric acid is the most suitable acid for maintaining this acidity; and
5. the hardening properties of a bath containing an excess of developer decrease with age.

Practical exhaustion tests with and without revival with acid made with 2 per cent and 3 per cent chrome alum baths have shown that:

1. as the degree of exhaustion increases, the acidity and hardening properties decrease;
2. the addition of sulfuric acid at regular intervals increases the hardening properties and prolongs the life of the bath;
3. with a 3 per cent chrome alum bath more uniform hardening properties are obtained with use than with a 2 per cent bath; and
4. more uniform hardening properties are also obtained at 85°F than at 70°F.

Based on these findings the following stop bath was proposed:

Kodak SB-3 Stop Bath

Chrome alum	30 g
Water to make	1 liter

When photographic films are immersed in this bath, the film should be agitated thoroughly for about 30 secs. The time of the immersion should be from 3 to 5 min. If the bath is not replenished with acid, discard the bath when its original color of blue-violet turns to yellowish-green, as the bath has lost its hardening properties. The swelling of the gelatin of the film may be suppressed by adding 60 g sodium sulfate to the SB-3 bath. This chrome alum-sodium sulfate solution is known as Kodak SB-4 stop bath.

The chrome alum should be added to water with a temperature lower than 150°F, or hydrolysis of the compound will make the solution more acid and diminish the hardening properties. The film must be agitated for the first 30 to 45 sec in order to avoid stains and streaks. Agitation is necessary to keep the alkali of the developer from precipitating a sludge of chromium hydroxide on the film surface. Any hardening or nonhardening fixing bath may be used after the chrome alum stop bath, but a hardening fixing bath is not necessary. The surface of the processed film should be carefully wiped after washing and before drying. This wiping is to remove any chromium scum that might be present. Once dried, this scum is almost impossible to remove completely.

Two stains may be encountered when using chrome alum stop baths: (1) a greenish-white scum of chromium hydroxide or basic chromium sulfite precipitated on the film surface and (2) an intense green staining of the gelatin of the emulsion layer. As already indicated, the deposition of the surface scum is best avoided by thoroughly agitating the film when it is first introduced into the chrome alum bath and by maintaining the stop bath in an acid condition (pH 3.0). Once the scum is formed, it may be removed from wet film by swabbing with moist absorbent cotton. The green gelatin stain, especially intense with high-temperature processing, may be removed, if desired, by immersion of the film in a solution of 5% potassium citrate or a 50% solution of potassium hydroxide, but these treatments destroy any hardening effect that the chromium had upon the gelatin.

Chromium causes gelatin to be less soluble by linking together two adjacent gelatin molecules that exist in the form of long, coiled chains.[15] The chromium forms a covalent bond to the carboxyl group of the amino acid of one gelatin chain and a coordinate bond to the amino group of the amino acid on another nearby gelatin chain. This intermolecular bonding makes the gelatin matrix less soluble—that is, it becomes hardened—and the gelatin of the emulsion layer becomes less susceptible to abrasion. The chromium ion, however, may link the carboxyl and amino groups of the same gelatin chain. This intramolecular bonding does not cause gelatin hardening. It has been estimated that less than 10% of the chromium linkages involve the crosslinking to two neighboring gelatin chains.[16]

The dependence on pH of chrome hardening may be explained by considering the requirements for crosslinking two gelatin chains. At the isoelectric point, gelatin molecules exist as fairly tight balls, unfolding or uncoiling as the pH moves away from the isoelectric point. J. Pouradier[17] has used this concept to explain "the difference in behavior of 0.85% gelatin solution treated with chrome alum at pH 4.75 and pH 4.0. In an isoelectric solution at this dilution, the ball-like molecules are at a distance from one another and intramolecular bridges are formed almost exclusively, bringing about a decrease in viscosity, whereas at pH 4.0 the molecules are sufficiently expanded for them to form intermolecular bridges in sufficient number to increase the cohesion appreciably."

Continued decrease in the pH of the gelatin would cause the molecules to uncoil still further, thus increasing the distance between the reactive groups on neighboring molecules. This would reduce the possibility of crosslinking. Chrome alum stop baths require careful control of pH for maximum gelatin hardening because of the requirements for forming the bridges. Although this crosslinking is a very stable form of molecular bridging, the treatment of chrome alum hardened gelatin with citric acid will cause the citric acid to complex and remove the chromium ions. The use of strong alkali also destroys chrome hardening, presumably by forming the less soluble hydroxide of the chromium. The use of either of these treatments, recommended in case of difficulties with chrome alum stop baths, negates the value of such hardening baths and should only be used in an emergency.

The scums and stains encountered with chrome alum hardening has led to the use of potassium alum stop baths for hardening. But potassium alum baths are almost as susceptible to precipitation difficulties. The pH must be acid to prevent the precipitation of basic aluminum sulfite or aluminum hydroxide. This is accomplished usually by the presence of acetic acid. Citric acid is also often added to prevent the precipitation of basic salts even though it may prevent maximum hardening. Richard B. Willcock[13] has given this formula for a potassium alum hardening stop bath:

Water	236.6 ml	Sodium citrate	5.7 g
Sodium sulfite	22.7 g	Potassium alum	22.7 g
Glacial acetic acid	17.0 ml		

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Chapter 13
The Fixing Process

I think I may very fairly claim the discovery of the hyposulphites as fixing agents, as I believe I was the first to call the attention of chemists to that class of salts and their peculiar habitudes, especially in relation to the insoluble salts of silver.

J. F. W. HERSCHEL[115]

Talbot did not patent my valuable fixer. Here I had the advantage of having published my use of hyposulphite of soda which Hodgson (a chemist at the Apothecaries Hall) made for me in 1837 when London did not contain an ounce for sale.

J. B. READE[116]

Sir John Herschel, in 1819, was probably the first to discover that hypo could dissolve the unreduced silver salts without attacking the metallic silver. However, it was not until 1837 that J. B. Reade used it in photography.

L. W. PHYSIOC[117]

Photographic materials must be treated to remove the unused silver salts from the emulsion layer. This elimination is necessary to prevent the darkening of the still light-sensitive silver halides not used to form the silver image. The opaque silver salts must be removed to make the developed image appear transparent on film base. This process of removing the remaining silver halides from the gelatin layer is called fixing; any solution that dissolves silver halide is a fixing bath regardless of its composition.

The chloride, bromide, and iodide salts of silver are almost insoluble in water. An extremely small number of silver and halide ions do dissolve in water, however, but once this number is in solution, no more ions from the crystals go into the solution. Silver ions in solution may unite with certain other ions to form a combined ion called a complex ion. The silver in the complex ion is no longer a free silver ion as before but loses much of its character. To replace the free silver ions that have been removed by complex ion formation, additional silver ions are released by the silver halide crystals. In this manner the almost-insoluble silver halide crystals may be dissolved by the continued removal of silver ions from solution by complex formation.

Such a slow process of solubilization of silver halide crystals may occur to some degree, but this is not thought to be the main mechanism of fixation. Solubilization of silver halide grains is believed to occur by adsorption of the silver complexing agent on the surface of the grain. If the affinity of the silver complexing agent for silver is greater than that of the halide ion for the silver ion of the crystal, then the complexing agent can combine with the silver ion, removing it from the structure of the crystal. The complex ion, if soluble, would pass into solution along with an equal number of halide ions. The surface of the grain would be etched away, making the crystal size grow smaller and smaller. (See Figure 1.)

Many compounds have been used to remove free silver ions from solution or to extract the silver ions from the lattice of silver halide crystals. This etching action actually begins during development. Some fine-grain developers contain small quantities of silver solvents such as ammonia or ammonium compounds, potassium thiocyanate, or sodium thiosulfate. Sodium sulfite is a constituent of almost every developer and is often used in considerable quantities. Sulfite forms the complex ion, $Ag(SO_3)_2^{3-}$, with silver ions in solution or removed from the surface of emulsion grains. Chloride, bromide, or iodide ions in solution may combine with silver ions and dissolve silver halide crystals. All of these silver solvents and many others, such as organic amines and organic sulfur compounds, may be used for fixation.

In a silver chloride crystal the attraction between the silver ion and the chloride ion is less than that between the silver ion and the bromide ion in a silver bromide crystal. Silver ions are attracted to iodide ions in silver iodide

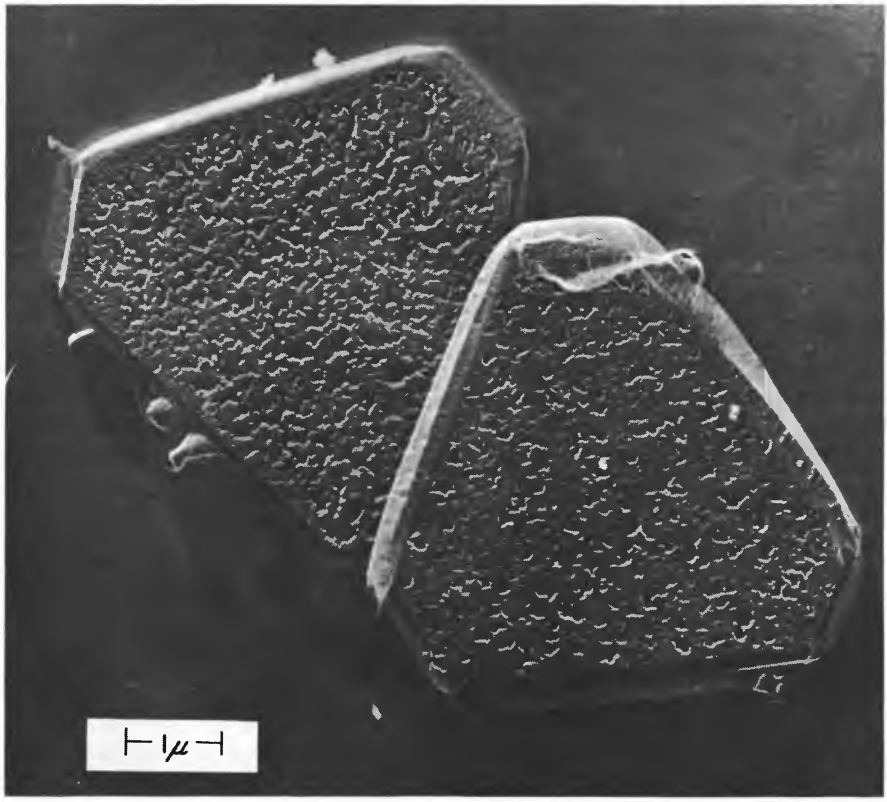


Figure 1. The etching of the surface by sodium thiosulfate is shown in this electron micrograph of large silver bromide grains. [J. F. Hamilton, L. E. Brady, and F. A. Hamm, *J. App. Physics*, 29: 80 (1958)]

more strongly than silver ions are attracted by bromide ions in silver bromide. Because of its weaker attraction between ions, silver chloride may be dissolved by a complexing agent that may not have sufficient affinity for silver ions to dissolve silver bromide, silver iodide, or mixed crystals of bromide and iodide. Ammonia or sodium sulfite, alone in solution or in combination, can readily dissolve silver chloride but only slowly attack silver bromide. Sodium thiosulfate or potassium cyanide solubilize silver bromide, but only the cyanide is efficient in dissolving silver iodide. Potassium cyanide—that is, the cyanide ion—has such a strong affinity for silver ions that it can dissolve silver sulfide, one of the least soluble of all silver compounds. Silver sulfide is often found in photographic stains, but the cyanide is a too toxic compound to be used to remove these stains. Concentrated solutions of iodide, forming the complex AgI_2^- ion with silver ions, have found use for the solubilization of silver sulfide stains.

Organic compounds containing nitrogen, sulfur, or phosphorus atoms are often effective as silver solubilizing agents. Organic compounds with unsaturated linkages of high electronegativity that occur between carbon atoms, especially acetylenic compounds, have sufficient affinity for silver ions to dissolve silver halide crystals. Activated methylene groups or thioether linkages in organic molecules also attract silver ions but may not be able to solubilize all of the halides of silver. Indeed, the variety of organic compounds that interact with silver ions is great, offering a wide range of compound characteristics. Thiosinamine, thiourea, cysteine, mercaptoacetic and mercaptobenzoic acids, thioglycerol, thiosugars, thiopyrimidines, and many other sulfur-containing organic compounds have been shown to be practical fixing agents.

Today, despite the very large number of complexing agents known to dissolve silver halide crystals in the emulsion layer, sodium and ammonium thiosulfate are used almost exclusively in practice to fix photographic films and papers. Both of these salts were reported by J. F. W. Herschel[1] in 1819 to dissolve silver chloride, so that the silver solubilizing action of these compounds, mistakenly called hyposulfites, was known before a photographic process had been invented. Hyposulfite of soda was a misnomer for the compound that we today call sodium thiosulfate, but the name "hypo" still is used to refer to the sodium or ammonium thiosulfates or the fixing bath containing these salts.

The Reverend J. B. Reade has been credited[2,3] with being the first (1837) to use thiosulfate to fix a photographic image. Herschel claimed to have fixed photographic images on January 29, 1839, about six months before the details of Daguerre's secret process were revealed. The high silver iodide content of the early photographic processes limited the use of the thiosulfates, because these compounds dissolve silver iodide rather slowly. Sodium thiosulfate was expensive and ammonium thiosulfate difficult to prepare and purify. Potassium cyanide, though an extremely deadly chemical if mishandled, was widely used during this period of photography. However, when the gelatin–silver halide emulsion began to be used from about 1880 on, sodium thiosulfate began to be the choice for fixing solutions. Today, thiosulfate fixing baths are universally used in all but a few specialized applications.

CHEMISTRY OF THIOSULFATE FIXATION

The chemistry of the thiosulfate fixing bath is complex, but some of the complexity was contributed by early investigators who attempted to isolate the series of silver thiosulfates that might be formed in solution. In 1933

Henry Bassett and John T. Lemon[4] established the four solid silver thiosulfate complexes that could definitely exist, agreeing in part with the earlier work by H. Baines.[5] However, it is now realized that all the solid compounds that may be isolated do not necessarily exist in solution during the fixing process.

Photographic fixation by sodium thiosulfate baths is currently thought[6,7] to involve the diffusion of the thiosulfate ion to the surface of the silver halide grain where it adsorbs, forming a complex ion consisting of one silver ion and one thiosulfate ion (monoargentomonothiosulfate ion, according to the nomenclature of Baines, or, more simply, silver thiosulfate ion). The sodium ion does not appear to have a significant role in the formation of the complex ion. This silver thiosulfate ion is not very soluble and it is retained on the surface of the silver halide crystal. If the number of thiosulfate ions in solution is limited, such as in an exhausted fixing bath, the silver thiosulfate ion may decompose, forming silver sulfide. In the presence of excess thiosulfate ions, however, the silver thiosulfate ion reacts with another thiosulfate ion, forming a complex with one silver and two thiosulfate ions. This complex ion is water-soluble and relatively stable, so that it may diffuse away from the surface of the silver halide grain. In solution, the complex ion of one silver and two thiosulfate ions may react with a third thiosulfate ion.

The reactions of fixation may be written

(1) $AgBr + S_2O_3^{2-} \longrightarrow [AgS_2O_3]^- + Br^-$

(solid) (solution) (adsorbed complex of low solubility and low stability) (from solid into solution)

(2) $(AgS_2O_3)^- + S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-}$

(adsorption complex) (solution) (leaving crystal surface and passing into solution)

(3) $[Ag(S_2O_3)_2]^{3-} + S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_3]^{5-}$

(solution) (solution) (solution)

As fixation continues, more of the free thiosulfate ions are combined into complexes. For every silver ion complexed, a halide ion is liberated from the crystal structure and passes into the solution. The concentration of halide ions will keep increasing in the fixing bath as the fixation proceeds. Eventually, the affinity for silver ions by the solubilized bromide and iodide ions in the solution will equal or exceed the affinity for silver ions by the remaining thiosulfate ions of the used fixing solution. At this point the

fixing bath cannot dissolve any more of the silver halide, because the excess of halide ions will reform silver bromide or silver iodide as fast as the crystals are dissolved. The fixing bath is said to be exhausted, even though free thiosulfate ions do exist in the solution.

It is undesirable to reach the exhaustion point of a fixing bath, because the lack of excess thiosulfate ions will mean that much silver thiosulfate (the one-to-one complex) will exist within the photographic material or will be adsorbed from solution, especially upon the paper fibers of photographic print materials. This complex of low solubility is not completely removed even by very thorough washing in water. The unstable complex, retained in the photographic material, will eventually decompose and attack and color the silver image.

Silver thiosulfate complexes, once in solution in the fixing bath, may dissociate into ions to a small extent:

$$\underset{\text{(solution)}}{Ag(S_2O_3)_2^{3-}} \rightleftharpoons \underset{\text{(solution)}}{Ag(S_2O_3)^-} + \underset{\text{(solution)}}{S_2O_3^{2-}}$$

$$\underset{\text{(solution)}}{Ag(S_2O_3)^-} \rightleftharpoons \underset{\text{(solution)}}{Ag^+} + \underset{\text{(solution)}}{S_2O_3^{2-}}$$

The silver ion released by the breakdown of the silver thiosulfate complex would be reduced to metallic silver in the presence of an active reducing agent. The formation of metallic silver is especially favored in the presence of any suitable nuclei that act as centers for the deposition of the metallic silver atoms. Metallic silver may be formed as a layer of dichroic fog on the surface of the emulsion layer if the fixing solution is allowed to become alkaline through overuse of the bath. Overexhaustion of the fixing bath allows the developing agents that are carried into the solution to reduce the free silver ions. Bassett and Lemon have reported that the decomposition of silver thiosulfate is accelerated by the presence of excess silver ions such as would most likely be present in a nearly exhausted fixing bath.

PRACTICE OF THIOSULFATE FIXATION

The old rule of fixing twice the emulsion clearing time was partly based on the idea that any insoluble silver thiosulfate formed during clearing would be converted to the water-soluble thiosulfate complexes during the additional time of treatment. If the thiosulfate is nearing exhaustion in a fixing bath,

more of the insoluble silver thiosulfate will be formed, because uncomplexed thiosulfate ions will not be in their normal excess. To make sure that sufficient excess thiosulfate ions are available to convert the silver thiosulfate to the water-soluble silver dithiosulfate ion, the use of a second fresh fixing bath has been suggested to follow the first used bath. This fresh second bath containing thiosulfate converts most, though not necessarily all, the silver thiosulfate to the silver dithiosulfate ion, which is then removable by washing with water.[9] However, water washing cannot remove all traces of thiosulfate and nonimage silver. It was also reported by A. E. Ballard and C. W.Zuehlke[10] that "under conditions which exist in an emulsion during fixing, a small amount of silver undergoes a chemical change, yielding a product which cannot be removed by a fresh fixing bath or a water wash. Some of this nonhalide silver probably exists as a silver-gelatin complex."

The solubilization and removal of the unused silver halide is essential for insuring the permanence of the silver image. When a silver bromide emulsion layer is immersed in a thiosulfate fixing bath, the turbidity of the silver halide salts soon disappears and the film becomes transparent; that is, the film has cleared. At this point of the fixation, according to Pierre Glafkides,[11] about 5% of the original silver bromide still remains. (A. W. Warwick[12] states that from 5 to 12% remains unchanged at the point of film clearing.) To reduce this amount of unchanged silver bromide to less than 0.25%, the fixation time is continued usually for twice the time to clear and often for more than twice the clearing time. The concept of clearing time, although difficult to estimate accurately, has been used as a handy measure of the effectiveness of silver complexing agents and the fixing baths that contain them.

It might seem advisable to fix films for much more than twice the time to clear in an effort to insure complete solubilization of the silver halide or the silver thiosulfate complex. Long immersion times in a fixing bath, however, must be avoided, especially with photographic papers.[13] Long periods of immersion of a photographic material in an acid hardening fixing bath may result in the thiosulfate or silver thiosulfate becoming so strongly bound to the gelatin of the emulsion layer, or the paper fibers of a photo paper, that washing will not remove these thiosulfates. Another danger of long fixing-bath immersions is the direct attack on the silver image by the combination of oxygen and the acid fixing bath. It is believed that oxygen from the air dissolves in the fixing bath and attacks the very finely divided silver particles of the image. Oxygen converts these metallic silver particles to silver ions by removing electrons. The silver ions are then complexed by the thiosulfate and removed, resulting in a loss of image silver. Fine-grained film and paper images are especially susceptible to image reduction by acid thiosulfate solutions. (See Figure 2.)

According to H. D. Russell and J. I. Crabtree,[14] "The extent of the reducing

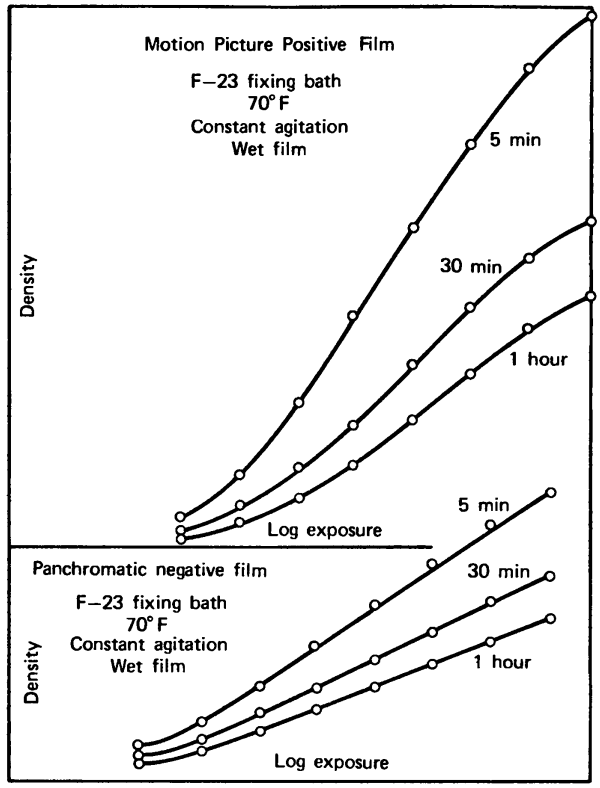


Figure 2. The loss in density of the silver image is shown for two films that were immersed up to 1 hr in Kodak F-23 fixing bath. The F-23 bath contained 300 g sodium thiosulfate pentahydrate, 17.5 g sodium sulfite (desiccated), 2 ml concentrated sulfuric acid, 32 g potassium chrome alum, and sufficient water to make one liter of solution. [H. D. Russell and J. I. Crabtree, *J. SMPE*, 18: 374 (1932)]

effect of fixing baths on the silver image during the progress of fixation is greater than has been generally supposed." This attack does not occur in alkaline thiosulfate solutions such as a fixing bath of 25% sodium thiosulfate with 1% anhydrous sodium carbonate. The rate of image reduction increases with the acidity, the degree of agitation, the temperature of the bath, and the freshness of the bath. Active acid fixing baths of high acidity may be used to reduce the contrast of photographic silver images. Avoiding any unintentional image reduction requires that the minimum fixing time be used and unnecessarily long immersion times, especially during the processing of photographic prints, be avoided.

In practice, the processor is most interested in the speed of fixation; usually, the shorter the time, the more desirable is the bath. The time of film clearing, or fixing, in thiosulfate solutions is dependent upon:

- Nature of the emulsion layer—grain size, halide content, silver coverage, amount of gelatin and/or polymeric vehicle, hardening and thickness of emulsion layer, and other factors.
- Activity of the thiosulfate—the kind of thiosulfate salt, the amount in the bath, and the degree of exhaustion of the bath are major factors affecting the fixing rate.
- Processing conditions during fixation—temperature and agitation of the solution—greatly influence the time of fixation.
- Miscellaneous factors—for example, the nature of the developer and stop bath used during the processing.

Nature of the Emulsion Layer

Fine-grain silver halide emulsions fix more rapidly than coarse-grained emulsions at the same silver coverage and emulsion thickness. Emulsion layers with lower iodide content are easier to fix in thiosulfate solutions than those with higher iodide content. Strongly adsorbed addenda in the emulsion layer, such as dyes and sulfur-containing compounds on the silver halide, may inhibit fixation. The nature of the gelatin, or the gelatin substitute, present in the emulsion layer can be a factor affecting fixing time as well as the thickness of the layer. Thick layers require longer for the thiosulfate ion to diffuse than do thin ones. The actual quantity of silver present (silver coverage) is a determining factor, too, as a longer time is required for the complexing reactions to occur when many silver ions are involved.[15]

Activity of the Thiosulfate

The kind of thiosulfate salt and its concentration are important in determining the rate of fixation. Ammonium thiosulfate fixing baths may clear film two to four times faster than similar sodium thiosulfate solutions.[16] Lithium thiosulfate produced solutions that fixed film in times that were intermediate between the sodium and ammonium thiosulfates. But potassium thiosulfate has been reported by K. Frank[17] and Walter Schramm[18] to be almost ineffective as a fixing agent. The reason for this behavior was that "the primary complex, i.e., the silver rich complexes of thiosulfate, are only sparingly soluble as potassium salts."[17]

The effect of the concentration of the thiosulfate salt has been the subject of some confusion, apparently because of the experimental techniques of the

scientists who studied the times of fixation. The published results of C. Welborne Piper (1913),[19] A. W. Warwick (1917),[12] S. E. Sheppard, Felix A. Elliott, and S. S. Sweet (1923),[20] Strauss (1925),[21] F. F. Renwick (1929),[22] and J. I. Crabtree and H. A. Hartt (1929)[15] unanimously agreed that as the concentration of sodium thiosulfate increased from zero quantity, the fixing time decreased until a concentration of about 20% was reached. The fixing time remained at about the same value until the thiosulfate concentration was about 40%. Increasing the thiosulfate concentration beyond this value required a longer and longer time to fix the film. On the basis of these findings, fixing baths of 30% sodium thiosulfate were suggested as the optimum thiosulfate concentration for the minimum fixing time. (See Figure 3.)

In 1942 W. T. Hanson, Jr.,[8] in the face of the unanimity of the acknowledged experts in the field of fixation, suggested that the time of fixation of a fine-grain and a coarse-grain photographic emulsion by sodium thiosulfate

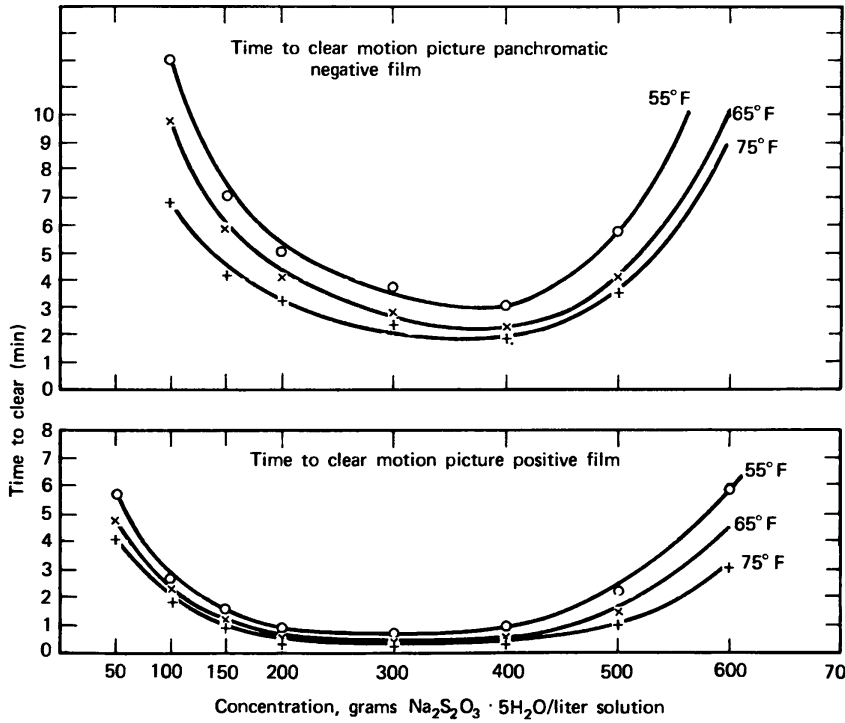


Figure 3. With dry film, the clearing time of the emulsion layer reaches a minimum when the concentration of sodium thiosulfate is 300 to 400 g/liter of solution. [J. I. Crabtree and H. A. Hartt, *Am. Phot.*, 23: 613 (1929)]

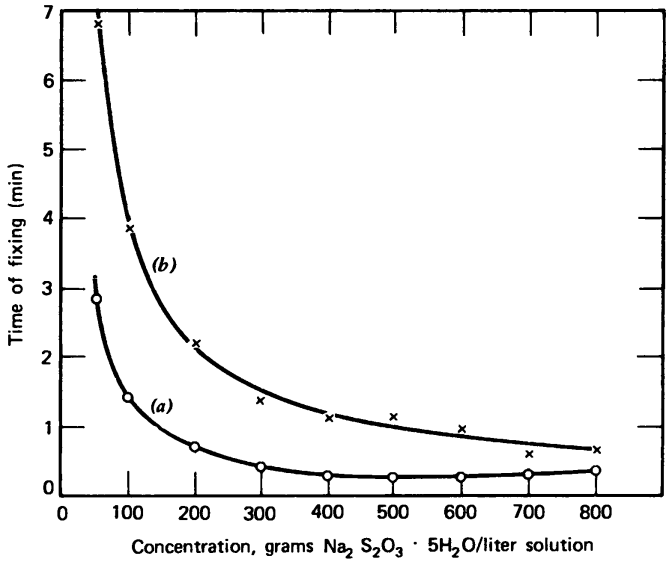


Figure 4. With wet film, increasing concentration of sodium thiosulfate decreased the time of fixing for either (*a*) a fine-grain film or (*b*) a coarse-grain film. [W. T. Hanson, Jr., *Am. Phot.*, 36: 22 (March 1942)]

decreased as the concentration of the thiosulfate was increased up to 70%. There was no optimum concentration at which the time of fixation was a minimum; rather, the greater the concentration of the sodium thiosulfate, the shorter the time to fix the emulsion. (See Figure 4.)

The next year Donald B. Alnutt[16] resolved this conflict of opinion. Either result may be obtained, depending upon whether dry or wet film is used to determine the time of fixation. Dry film will not swell easily in the solutions containing the higher concentrations of the thiosulfate salt. This limits the penetration of the thiosulfate ion, and fixing times become longer and longer as the thiosulfate concentration rises above 40%. In most photographic processing, however, the emulsion layer is wet and swollen when it enters the fixing bath. The thiosulfate at high concentrations in the bath undergoes dilution as it enters a wet film swollen with water. This diluted concentration of thiosulfate penetrates into the gelatin layer easily and clears the film more quickly. As H. Baines[7] has sagely remarked, all the earlier scientists "fell into the error of assuming without question that what happens with dry film in a laboratory will happen with wet film in a darkroom."

The extent of reaction of the thiosulfate ion with silver influences the time of fixation. In a fresh bath the thiosulfate ions have not reacted with any silver and all are available. As the thiosulfate ions complex with silver ions,

two or three thiosulfates are combined to solubilize one silver ion. As fewer and fewer thiosulfate ions exist in the free ion state, the fixing time becomes longer and longer. More silver thiosulfate is formed on the silver halide surface, and it takes longer before another thiosulfate ion becomes available to solubilize the first complex of silver with the thiosulfate. The degree of exhaustion of the available thiosulfate ions can play a role in lengthening the film clearing time, although other factors also contribute.

Processing Conditions During Fixation

Both the temperature of the fixing bath and the agitation used during immersion of the film are important factors that affect the time of fixation. Increasing the temperature or increasing the degree of agitation shortens the time of fixing. An increase in temperature has the effect of increasing the rate of diffusion of the thiosulfate into the gelatin layer, increasing the swelling of the gelatin layer, and increasing the rate of chemical reaction of the silver halide and the thiosulfate. With normally hardened emulsion layers, the rate of fixation is slow below 65°F and the swelling of the gelatin may become excessive above 75 to 80°F. J. I. Crabtree and G. E. Matthews[23] reported that lowering the fixing-bath temperature from 75 to 55°F (24 to 13°C) required the fixing time to be doubled for fixing roll film. The optimum fixing temperature lies between 65 to 75°F, essentially the temperature of the developer used in normal development. With highly hardened emulsions or with prehardened emulsions (hardened in a separate bath before development), higher fixing temperatures yield shortened fixing times. The rate of hardening given by an acid hardening fixing bath increases with temperature unless the gelatin layer has been swollen excessively before entering the bath.

Agitation in the fixing bath speeded up the time of fixation.[23] With agitation, the time of fixation dropped from 15 min at 60°F (15°C) to 5 min at 75°F (24°C). Without the agitation, fixation took 20 min at the lower temperature and 7 min at the higher temperature. Higher degrees of agitation and higher temperatures combine to shorten fixing times.

According to the early work of S. E. Sheppard and C. E. K. Mees,[24] agitation not only helped to increase the rate of fixation but modified the course of the reaction. Fixation involves a penetration of the gelatin by the solution to the surface of the silver halide crystal, and the chemical reactions between the thiosulfate ion and the silver ion. With a sufficient supply of thiosulfate ions, the speed of fixation is determined not by the chemical reaction but by the diffusion time to reach the grain surface. Agitation of the solution sweeps new solution to the emulsion surface and removes the reacted products, effectively reducing the diffusion path outside of the emulsion surface. Sheppard and Mees summarized their findings: "Stirring

greatly increases the velocity of the reaction. The induction period is less, and it appears that after some time the available surface is increased, the rate becoming proportional to the total mass or density of AgBr present."

Rapid fixation is obtained when thin layers of moderate hardening are treated in a fixing solution at high temperature and with high agitation. Rapid fixation is diffusion controlled, so the effects of high temperature and high agitation, although significant, are limited.

Miscellaneous Factors Affecting the Time of Fixation

The time of fixation by thiosulfate solutions is influenced by the presence of other salts in the bath. For monobath use, for example, sodium thiosulfate was found to require a considerably longer time to clear film in the presence of the other monobath processing chemicals, even excluding the developing agents, than when the same quantity of sodium thiosulfate was used alone at the same pH.[25] The alkalinity of the developer and the acidity of the stop bath may also affect the fixing time but, although there is some disagreement, the degree of hardening of the film is not thought to materially change the time to fix.

The carrying over of chemicals from the developer, such as strongly adsorbed antifoggants in the emulsion layer, or the leaching of agents from the emulsion layer, such as organic stabilizers or halide ions, may have a definite retarding effect on the rate of fixation. Potassium ions (from potassium salts in the developer) slow the rate of fixation by forming less-soluble potassium thiosulfates. The accumulation of iodide ions in the fixing solution has a large restraining effect on thiosulfate fixation. The presence of iodide in the fixing bath is one of the major reasons that thiosulfate solutions are said to be "exhausted." Although the film will still clear, the time becomes very long. W. Schramm[18] concluded, "Although it is said that the sodium halides do not affect the saturation limit of the fixing bath, they prolong the time of fixing, the chloride the least, the bromide more, and the iodide most, in the approximate ratio of 1:10:120." However, the presence of small quantities of iodide (0.2 g/liter) in a thiosulfate fixing bath has been found beneficial for improving the permanence of the silver image.[26]

COMPOUNDING FIXING BATHS WITH SODIUM THIOSULFATE

A water solution of sodium thiosulfate is adequate for some fixing purposes; in fact, a 20% solution of sodium thiosulfate is recommended for the fixing of extremely finely divided silver images. Such a bath has a very limited life,

because the photographic material, even though rinsed after development, may still carry in some of the constituents of the developer. The presence of developing agents in a thiosulfate solution may result in the reduction of free silver ions in solution, producing dichroic fog deposits on the film surface. In time the developing agents will oxidize, causing the thiosulfate solution to darken. These oxidation products of the developing agent can stain the gelatin of the emulsion layer. An intermediate acid stop or rinse bath would destroy the alkalinity of the absorbed developer in the emulsion layer, thus preventing the developing action from occurring in the fixing solution. However, as the acid from the stop bath is carried into the thiosulfate solution, a point of acidity will be reached where sulfur will be precipitated from the thiosulfate.

The Chemistry of Acidity Control

The addition of an acid to a thiosulfate solution is essential to neutralize any alkalinity carried over in the emulsion layer of the photographic material. Acidity is also necessary if alum hardening agents are to be present in a fixing bath. When acid is added to a sodium thiosulfate solution, thiosulfuric acid is formed. This acid may not decompose immediately if the conditions are mildly acid. Soon, however, the thiosulfuric acid breaks down to form sulfurous acid and colloidal sulfur.

$$H_2S_2O_3 \longrightarrow H_2SO_3 + S$$

If a photographic material is fixed in a bath that is precipitating sulfur, some of the sulfur particles will be formed in the gelatin layer of the emulsion.[27] Washing with water will not remove this precipitated sulfur. In time, the sulfur may react with the silver image, causing the image to brown and fade (sulfiding of the image).

The exact nature of the decomposition of thiosulfuric acid depends upon the quantity of acid present. According to E. Gruenthal,[28] a chain of reactions occur that involve the by-products of the decomposition of the thiosulfuric acid.

$$\begin{aligned}
H_2S_2O_3 &\longrightarrow H_2SO_3 + S \\
H_2SO_3 &\longrightarrow H_2O + SO_2 \\
5S + 5SO_2 + 2H_2O &\longrightarrow 2H_2S_5O_6 \\
S_5O_6^{2-} + 2SO_3^{2-} &\longrightarrow S_3O_6^{2-} + 2S_2O_3^{2-} \\
S_3O_6^{2-} + H_2O &\longrightarrow SO_4^{2-} + S_2O_3^{2-} + 2H^+
\end{aligned}$$

The Gruenthal concept postulates that the sulfurous acid, formed by the initial decomposition of the thiosulfuric acid, is unstable under acidic conditions, yielding sulfur dioxide. The sulfur dioxide then reacts with the sulfur to form pentathionic acid, which decomposes to produce trithionic acid and more thiosulfuric acid. The trithionic acid is also unstable, forming sulfuric acid and more thiosulfuric acid. The presence of thiosulfuric, trithionic, or pentathionic acid residues near a silver image in an emulsion layer will eventually result in the fading of the image because of presence of sulfur formed when the acids decompose. Other mechanisms of reaction have been postulated.[29]

In acid solution, sodium thiosulfate is converted to the unstable thiosulfuric acid, which decomposes because the sulfur is only loosely bound. This reaction is a reversible one, however, as excess sulfurous acid will combine with any sulfur formed to reform the thiosulfate. The addition of sulfurous acid to a thiosulfate fixing bath will prevent the precipitation of sulfur when the bath is acidified. Sulfurous acid, the water solution of sulfur dioxide gas,

$$H_2O + SO_2 \rightleftharpoons H_2SO_3$$

is unpleasant to use because the reversible reaction discharges pungent sulfur dioxide gas into the air.

The exact proportions of sodium sulfite and sulfuric acid may be used to provide the sulfurous acid.

$$Na_2SO_3 + H_2SO_4 \rightleftharpoons H_2SO_3 + Na_2SO_4$$

This avoids the use of sulfur dioxide gas to form the sulfurous acid, but sulfur dioxide can be evolved from the decomposition of the sulfurous acid in solution. Fixing baths entirely acidified with sulfurous acid are so acidic that some silver of a finely divided image may be bleached. Sulfurous acid is not stable in the presence of atmospheric oxygen, forming sulfuric acid ($H_2SO_3 + O \rightarrow H_2SO_4$). A thiosulfate fixing bath acidified solely with sulfurous acid will, in time, deposit sulfur as the free sulfite ion is converted to the sulfate ion by air oxidation.

A chemical source of sulfurous acid and sulfite combined is found in the acid sulfites. Sodium metabisulfite may be regarded as sodium sulfite with sulfur dioxide added.

$$Na_2SO_3 + SO_2 \longrightarrow Na_2S_2O_5$$

Sodium bisulfite ($NaHSO_3$) is the half-neutralization product of sulfurous acid with sodium hydroxide.

$$H_2SO_3 + NaOH \longrightarrow NaHSO_3 + H_2O$$

As R. B. Willcock[9] has pointed out, sodium bisulfite may be considered as a hydrated form of metabisulfite.

$$NaHSO_3 + NaHSO_3 \longrightarrow Na_2S_2O_5 + H_2O$$

Sodium metabisulfite is photographically the same as two molecules of sodium bisulfite and one molecule of water. Willcock concluded, "In the case of the metabisulphites of sodium and potassium, equivalent weights of the three substances will give the same amount of sulphurous acid when dissolved in equal quantities of water. That is to say, approximately equal acidity is provided for by 190 parts by weight of sodium metabisulphite, 222 parts of potassium metabisulphite and 208 parts of sodium bisulphite, but, for most purposes, the three salts may be substituted one for another."

Acid sulfites avoid the problem of overacidification of the fixing bath. Sodium sulfite may then be used as a buffer or to reduce the acidity of the solution, as might be desirable for warm-weather processing. Such a simple nonhardening fixing bath was proposed by Crabtree and Hartt in 1929.[15]

Sodium thiosulfate	250 g
Sodium sulfite, desiccated	10 g
Sodium bisulfite	25 g
Water to make	1 liter

This formulation is essentially the same as the currently recommended Kodak fixing bath F-24.

Kodak Fixing Bath F-24

Water, about 125°F (50°C)	500 ml
Sodium thiosulfate pentahydrate	240.0 g
Sodium sulfite, desiccated	10.0 g
Sodium bisulfite	25.0 g
Cold water to make	1.0 liter

Dissolve chemicals in the order given. The temperature of the developer, stop or rinse bath, and wash water should not be higher than 68°F (20°C).

Fixing bath F-24 may be used for films, plates, or papers when no hardening is needed. The reserve acidity of the sodium bisulfite is insufficient to maintain the pH of the solution with continued use. If such a fixing bath is to have a long life, its acidity must be maintained by either continuous addition of sodium bisulfite solution or replenishment at regular intervals.

Sulfurous acid may be liberated from sodium sulfite by a suitable acid, eliminating the need for a bisulfite or a metabisulfite in the bath. But the choice of the liberating acid is very limited. H. D. Russell and J. I. Crabtree[30] have found that most organic acids were unsuitable but concluded that acetic, propionic, and butyric acids could be used. Strongly ionized acids, such as sulfuric, cause sulfurization of the thiosulfate in the solution. Sulfamic acid (HSO_3NH_2) has been patented for use in fixing baths (British Patent 534,409). The use of a half-neutralized sulfuric acid (sodium hydrogen sulfate) to cut down the acidity was suggested by D. P. Woosley and K. G. A. Pankhurst.[31]

Sodium hydrogen sulfate is a stable, nondeliquescent compound that may be packed in dry fixing-bath compositions. A suitable formulation, as suggested by Woosley and Pankhurst, has the following composition.

Sodium thiosulfate, crystals	350 g
Sodium sulfite, anhydrous	15 g
Sodium hydrogen sulfate	15 g
Water to make	1 liter

Dissolve the thiosulfate, then the sulfite in 600 ml of water at 125°F; dissolve the sodium hydrogen sulfate in a separate 200 ml of water at 125°F. Cool both solutions to 70°F. Add the sodium hydrogen sulfate solution slowly with stirring to the thiosulfate-sulfite solution. Add cold water to make the final volume of one liter. The solution pH is 4.8.

Harold D. Russell and Lowell E. Muehler in British Patent 2,378,248 combined the acid sulfate with the salt of an organic acid containing two to four carbon atoms to generate the free carbon acid. A commonly used free carbon acid is acetic acid, but this compound is a liquid. Both the acid sulfate and the salt of the organic acid were solids, so packaging of an acid hardening fixing bath was simplified. A single-solution fixing bath of this type had the formulation

Sodium thiosulfate (crystals)	240.0 g
Sodium bisulfite	15.0 g
Sodium acetate (desiccated)	20.0 g
Boric acid	7.5 g
Sodium acid sulfate (20% solution)	75.0 ml
Potassium aluminum sulfate (crystals)	15.0 g
Water to make	1.0 liter

The sodium acid sulfate solution may be made by adding anhydrous sodium acid sulfate to water (200 g/liter) and cooling the solution before adding the required volume to the cool solution of the fixing bath.

ACID HARDENING THIOSULFATE FIXING BATHS

Most modern fixing baths in general use contain a substance to make the gelatin of the emulsion layer of films and papers less susceptible to abrasion or to melting at higher-than-normal processing temperatures. Acid hardening thiosulfate fixing baths contain five ingredients: silver complexing agent, acid, preservative, hardening agent, and buffer.

Silver Complexing Agent

In practice, either sodium or ammonium thiosulfate is used as the silver solvent in today's fixing baths. For most purposes, sodium thiosulfate fixes sufficiently rapidly to be satisfactory. Sodium thiosulfate baths also are to be preferred for fixing photographic prints, as there is less danger of image bleaching than with ammonium thiosulfate baths. It was found by H. G. Morse[32] that a print left in an ammonium thiosulfate fixing bath for more than 5 min may suffer appreciable bleaching of the image, especially if the image is very fine grained. However, the more rapid rate of fixing of ammonium thiosulfate solutions has led to their adoption in automatic processing machines, in kits for color processing, and in many other of today's photographic processes where there is a need for rapid access to the recorded image.

Acid

The acid acts as a means to stop image formation, thus improving image uniformity, by neutralizing any developer alkali carried over into the fixing solution. Developing agents are less susceptible to oxidation in acid solution, so the oxidized forms do not color the solution and stain the photographic material immersed in it. An acid fixing bath stops the developing activity from continuing within the fixing solution, resulting in a reduction of silver ions from solution as a deposit on the surface of the photographic emulsion. Acid is needed in the fixing bath because alum hardeners require moderate acidity to be effective in their action upon the gelatin.

Almost any acid can act as an alkali-neutralizing agent. Organic acids such as acetic, citric, formic, diglycolic, oxalic, maleic, malic, tartaric, and others have been tried, as these acids are not as strongly acidic as inorganic

acids, thus avoiding the tendency of strong acids to precipitate sulfur from thiosulfate solutions. Most of these solid organic acids react with the aluminum from potassium alum to form compounds that are not efficient gelatin hardening agents.[20]

Acetic acid exists in solution mostly in the form of molecules, supplying free hydrogen ions slowly as they are used up. These unionized acetic acid molecules constitute a large reservoir of acid that is available for the neutralization of alkali that may reach the solution. Strong acids, such as sulfuric acid, supply almost all their hydrogen ions immediately upon being dissolved in water. Acetic acid, because it avoids the strong acidity of inorganic acids, is generally present in acid hardening fixing baths. But, as noted by J. I. Crabtree and H. A. Hartt,[15] "Much is still to be desired from the standpoint of a perfect acid for this purpose."

Preservative

The preservative is usually sodium sulfite. Its function is to prevent sulfur deposition from the thiosulfate in the acidic solution. As already indicated, the presence of excess sulfite ion reverses the decomposition of thiosulfuric acid. The sodium sulfite also helps prevent discoloration of the fixing solution by reacting with the oxidized forms of the developing agents that might be present. A source of sulfite ions has been present in acid thiosulfate fixing solutions ever since 1889, when A. Lanier[33] discovered that sulfur precipitation could be avoided by combining the acid with sodium bisulfite before adding the acidic solution to the thiosulfate solution.

Hardening Agent

The gelatin of the emulsion layer swells when immersed in the developer or stop bath or the fixing bath, but the salts in the developer and the fixing bath limit the extent of the swelling. The short time of immersion in a stop or rinse bath prevents excessive swelling during this step of the processing cycle. During the final water wash, however, the unrestrained gelatin of the emulsion layer may swell and soften excessively, increasing the danger of physical damage to the gelatin layer. (See Figure 5.) Temporary antiswelling agents, such as sodium sulfate, limit swelling in the processing solutions that contain such agents but are of little value during the subsequent washing of the photographic material. Permanent, nonreversible toughening of the gelatin is necessary to limit the swelling of the gelatin.

Some of the most useful gelatin hardeners are bifunctional organic molecules that form strong crosslinks between the gelatin chains. Such crosslinks

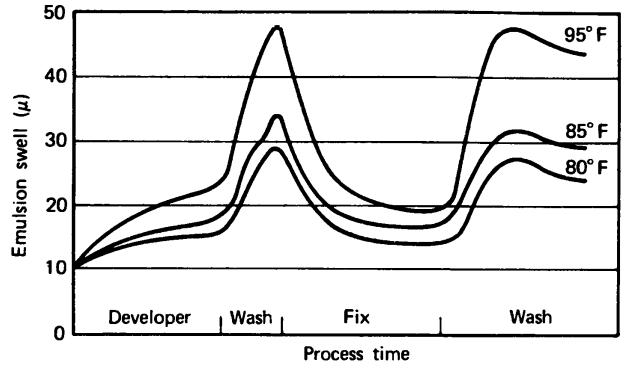


Figure 5. The emulsion swell of Recordak Micro-File film, Type 5454, illustrates the increase in swelling that occurs during water rinse or wash cycles. Note that the temperature of processing also influences the extent of emulsion swell. [Lloyd E. West, *Phot. Sci. and Eng.*, 9 (6): 402 (1965)]

limit the swelling of a hardened gelatin layer and raise its softening point. Many of these compounds, such as aldehydes, quinones and other developer oxidation products, tannin, and other substances, are effective crosslinking agents only in neutral or alkaline solution. Such compounds would be useful in developers or monobaths but are not of value in acid fixing solutions.

In acid solution certain inorganic metallic ions have a strong permanent hardening action upon gelatin helices. The salts of aluminum, chromium, iron, and zirconium are effective gelatin hardeners in acid solution. Iron may react with developing agents, or their oxidation products, to produce very dark-colored solutions. The salts of aluminum are to be preferred: they are colorless, easily water-soluble, and do not react with developing agents to produce colored compounds. Many salts of aluminum, such as the chloride or nitrate, may hydrolyze in water to precipitate aluminum sulfite in the presence of the sulfite ions of the developer or the fixing bath. The double salts of aluminum sulfate with sodium or potassium sulfate, called alums, yield a clear solution in the presence of sulfite. These double salts containing aluminum, called sodium or potassium alum, have the formulas:

$$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \quad \text{and} \quad K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O.$$

Potassium alum is the common alum used in acid hardening sodium thiosulfate fixing baths. Chrome alum, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, has been used as a gelatin hardener but is not as satisfactory as potassium alum. Ammonium alum, $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, may be used but evolves ammonia gas if the fixing bath should become alkaline during use.

Buffer

Alum-containing fixing baths harden gelatin over only a very limited range of acidic solution. Sheppard, Elliott, and Sweet[20] concluded that "for maximum hardening the acid fixing bath should have a considerable quantity of organic acid, and as large an amount of aluminum or chromium salt as is consistent with maintaining a pH = 4 or slightly greater. Acid making the pH = 3 is unsafe, while acidity pH > 5, while it may not precipitate alumina, will give poor hardening."

Fixing baths need to be carefully buffered against pH change during use. The hardening properties of potassium alum exist over a very limited range of acidity. Too low a solution acidity will precipitate sulfur from the thiosulfate; too high a pH causes the hardening action to become ineffective because of the precipitation of aluminum sulfite and aluminum hydroxide.

Acid hardening sodium thiosulfate fixing baths consist essentially of a neutral water solution of the thiosulfate and an acidified water solution of the alum. Hardening formulations have been compounded for addition to neutral thiosulfate solutions, so that both types of fixing bath can be obtained with a single thiosulfate solution. A typical fixing bath composition is the F-2 formula given by H. D. Russell and J. I. Crabtree.[30]

F-2 Fixing Bath

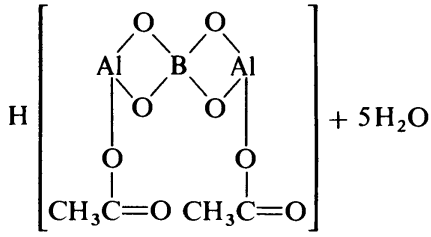
Water	1 liter
Sodium thiosulfate, crystal	240 g
When dissolved, add	
Water	50 ml
Sodium sulfite, desiccated	3 g
Acetic acid, 28%	18 ml
Potassium alum	6 g

The F-2 fixing bath sludged at pH 4.8, ending its useful hardening life. The addition of a minimum concentration of 5.0 g/liter of boric acid was found to extend the useful hardening life of the bath to a pH of about 6. This represents an increase in the sludging and hardening life of three to four times. In addition, when boric acid is present in the solution, sodium acetate may be substituted for part of the acetic acid. This reduces the evolution of sulfur dioxide when high concentrations of sodium sulfite and acetic acid are necessary in the bath.

Any boron compound which exists in an acid solution as the oxygen acid of boron may be used in place of boric acid. Glycol borate, glycerol borate,

and esters of boric acid may be used. Boron triacetate may be substituted in equivalent quantity for both the acetic acid and the boric acid of a fixing-bath formula. Borax and salts of oxygen acids of boron, such as sodium metaborate (Kodalk), require that an additional acid be added in sufficient quantity to form boric acid. The nonsludging properties of boric acid–thiosulfate fixing baths containing potassium alum have been ascribed to the formation of complex ions between the acetic acid, boric acid and the alum. Such a complexing reaction is thought to involve the following reaction.

$$2Al(OH)_3 + 2CH_3COOH + H_3BO_3 \longrightarrow$$



$$+ 5H_2O$$

The nonsludging properties are due to the presence of both the acetate and borate ions. Minimum concentration of boric acid should be 5 g/liter and of glacial acetic acid 10 ml/liter of fixing solution.

To maintain the buffered acidity needed for a potassium alum hardening fixing bath, the buffering components consist of acetic acid and/or acetate salt with a suitable organic acid. The presence of sodium sulfite helps improve the buffering action. The boric acid helps the buffering and, as well, helps to extend bath life by its antisludging action in cooperation with the acetate ion. These practical findings were utilized in 1933 by H. D. Russell and J. I. Crabtree to compound an improved fixing bath. This bath was the forerunner of the Kodak F-5 fixing bath that is still widely used as a general-purpose fixing solution for both films and papers:

Kodak Fixing Bath F-5

Water, about 125°F (50°C)	600 ml
Sodium thiosulfate pentahydrate	240.0 g
Sodium sulfite, desiccated	15.0 g
Acetic acid, 28%	48.0 ml
Boric acid, crystals	7.5 g
Potassium alum	15.0 g
Cold water to make	1.0 liter

Use crystalline boric acid instead of powdered boric acid, which is slow to dissolve. Fix prints from 5 to 10 min in a freshly prepared bath, or film or plates from 10 to 20 min. It is inadvisable to fix paper and film in the same solution.

The F-5 fixing bath formula can be made as a two-solution version: (1) one solution containing 30% sodium thiosulfate and (2) the other solution the buffering and hardening compounds. The following is a stock solution of the buffering and hardening constituents needed to prepare Kodak fixing bath F-5 using the two-solution method:

Kodak Hardener F-5a

Water, about 125°F (50°C)	600 ml
Sodium sulfite, desiccated	75.0 g
Acetic acid, 28%	235.0 ml
Boric acid, crystals	37.5 g
Potassium alum	75.0 g
Cold water to make	1.0 liter

Again, use crystalline boric acid instead of powdered boric acid, which is slow to dissolve.

After dissolving the chemicals in the order listed in the formula, add one part of the cool stock hardener solution slowly to four parts of the cool 30% sodium thiosulfate solution. Stir the thiosulfate solution rapidly during the addition of the hardener stock solution.

Sometimes the pungent odor of sulfur dioxide given off by the F-5 solution may be objectionable, especially in small darkrooms during warm weather or for any high-temperature processing. At a small sacrifice in hardening, the odor can be greatly minimized by substituting twice the weight of sodium metaborate (Kodalk or Kodalk balanced alkali) for the boric acid, which is eliminated. This fixing-bath modification, called Kodak fixing bath F-6, is almost free of sulfur dioxide odor, and the presence of the metaborate also helps improve the washing out of the thiosulfates from the emulsion layer. However, the F-6 fixing bath should follow an acid stop bath to obtain the full useful life of the bath without sludging.

CHROME ALUM FIXING BATHS

Chrome alum fixing baths are capable of a very high degree of hardening of gelatin, especially useful with high-temperature processing but possibly

excessive for hardening needed at normal temperatures. Some of the characteristics of solutions of chrome alum were described under stop baths. The hardening given by chrome alum solutions is decreased when the solution alkalinity rises due to the addition of alkaline developer or sodium bisulfite. The solution color changes from violet-purple to green. The green form has been reported to be unable to harden gelatin, but this was because of a failure to adjust pH. The presence of acetic, boric, citric, and other acids also decreases the hardening action of chrome alum baths.

Chrome alum solutions may be revived by adding sulfuric acid, changing the green solution to violet. However, the amount of sulfuric acid must be carefully controlled to avoid sulfurization or blistering of the gelatin emulsion layer. The formation of basic chromium salts is believed necessary before gelatin may be hardened. Organic acids such as acetic, citric, tartaric, and others prevent the formation of these salts. The presence of these acids in a thiosulfate fixing bath results in an initial loss of hardening by the chrome alum and accelerates the loss of hardening upon keeping the bath, whether used or not.

J. I. Crabtree and H. D. Russell[34] found that the maximum degree of gelatin hardening is obtained when the acidity of the chrome alum solution lies between pH 3.8 to 4.0 for neutral or well-washed film and between pH 3.0 and 3.8 for alkaline film. The acidity of 2 or 3 % chrome alum solutions is about pH 3.2, so these solutions would not be effective for neutral or water-rinsed gelatin emulsion layers. According to Crabtree and Russell, "A maximum degree of hardening results when the solution in contact with the gelatin film has a definite basicity or alkalinity resulting after the acid in the fixing bath has neutralized the alkali in the developer that is retained by the film. Since the acidity of a fixing bath or stop bath changes with use, its hardening properties change also."

For high-temperature processing, chrome alum stop baths or chrome alum fixing baths may be necessary, because a higher degree of gelatin cross-linking is obtainable than with potassium alum solutions. Probably the best choice would be a chrome alum stop bath followed by a potassium alum fixing bath. This would provide a more reliable and uniform degree of gelatin hardening with use than would be provided by a chrome alum fixing bath with a high concentration of alum.

At normal temperatures of processing, chrome alum baths may provide almost too much gelatin hardening, so that a thin, upper layer of the gelatin is highly hardened but the underlying gelatin is unhardened. This case-hardening of gelatin by chrome alum has resulted in some spectacular disasters, as the gelatin layer of the emulsion can slide off the film base. For example, in his book, *The Photographic Negative* (Vol. 2, p. 345), Herbert C. McKay mentioned that "The memory still lingers of sixteen hundred feet

of chrome-hardened motion-picture emulsion slipping from the celluloid base into a mass of sludge in the bottom of the tank."

The hardening action of potassium alum fixing baths is of a moderate degree, and this degree of hardening is maintained to a better degree with use. Generally, potassium alum fixing baths are now widely used for photographic processing at normal temperatures. Chrome alum fixing baths are used on those other occasions where additional hardening is needed.

The F-23 chrome alum fixing-bath formula was devised by J. I. Crabtree and H. D. Russell.[34]

Kodak Chrome Alum Fixing Bath F-23

Solution A	
Sodium thiosulfate pentahydrate*	240 g
Sodium sulfite, desiccated	12.5 g
Water to make	750 ml
Solution B	
Water	150 ml
Sodium sulfite, desiccated	5 g
Sulfuric acid, 5% solution†	40 ml
Potassium chrome alum	32 g
Water to make	250 ml

* Increasing the thiosulfate concentration to 300 g/liter of mixed solution will provide a bath which fixes more rapidly.

† To make a 5% sulfuric acid solution, add one part of concentrated sulfuric acid slowly and with stirring to 19 parts by volume of cold water. NOTE: Add the acid to the water, or explosive spattering of acid solution is liable to occur.

Cool solution A to 70°F after the constituents have dissolved. Make solution B separately, adding the compounds in the order listed. Cool solution B to 70°F. Then add solution B to solution A while stirring solution A vigorously. Unless solution A and solution B are cool when mixed, the bath will sulfurize.

Mixing conditions for chrome alum fixing baths are especially important. D. P. Woosley and K. G. A. Pankhurst[31] also stressed that the chrome alum

must be dissolved in cool water (70°F) before being added to the sodium thiosulfate–sodium sulfite solution at the same 70°F temperature. Dissolving chrome alum in hot water caused much of its hardening action to be lost. These investigators were able to formulate chrome alum fixing baths with sodium hydrogen sulfate that produced a high degree of hardening. A combined chrome alum-potassium alum fixing bath for general use, including the fixation of double-coated X-ray film, had the following composition (pH = 4.0):

Potassium Alum-Chrome Alum Fixing Bath for General Use

Sodium thiosulfate (crystalline)	350 g
Sodium sulfite, anhydrous	20 g
Sodium acetate	15 g
Sodium hydrogen sulfate	20 g
Potassium alum	15 g
Chrome alum	10 g
Water to make	1 liter

RAPID SODIUM THIOSULFATE FIXING BATHS

Immediate access to view a recorded image is often necessary in photography, particularly in the production of radiographs, oscillographs, computer printout, newspaper photography, military applications, and many other modern uses. Rapid development is obtainable in seconds, but fixing is a slow, time-consuming operation. Speeding up the action of fixing baths must involve increasing the rate of diffusion to increase the supply of thiosulfate ions at the surface of the silver halide crystal, increasing the rate of reaction between thiosulfate and silver ions, or increasing both rates. Both the rates of thiosulfate diffusion through gelatin and the rate of chemical reaction have been studied.

The rates of penetration of ammonium, lithium, potassium, and sodium thiosulfate into dry film were found by D. C. Shuman and F. Grum[35] to be the same, apparently limited by the time needed for the gelatin to swell. With films that were preswollen, however, the rate of penetration increased in the order, $Li_2S_2O_3 < Na_2S_2O_3 < K_2S_2O_3 < (NH_4)_2S_2O_3$, for 0.065 *M* solutions. If the rate of diffusion of lithium thiosulfate is assigned a value of 1, then sodium thiosulfate has a value of 1.8, potassium thiosulfate a value of 2.2, and ammonium thiosulfate a value of 2.3. These investigators concluded, "When a model is chosen for studying the clearing rates such that emulsion

swelling and chemical reaction are rapid, diffusion is rate-controlling and the rate of clearing depends on the cation type. The order of increasing rate of clearing is identical with the order of the increasing rate of penetration of the thiosulfates in gelatin films and is also identical with the order of increasing diffusion coefficients."

Increasing the rate of diffusion of the thiosulfate ion through gelatin is only one part of the problem of shortening the time for fixation. When the double-negative-charged thiosulfate ion nears the surface of the silver halide crystal, the ion must still penetrate against the repulsion of the negative charge barrier that surrounds the crystal. The negative potential barrier that surrounds the crystal is the result of adsorbed negatively charged ions that are attracted by the positively charged silver ions in the surface of the crystal.

The structure of the adsorbed layer on the crystal surface can be modified by treating the surface with a positively charged ion (cation) that is capable of adsorption on the crystal surface. When enough positive ions are adsorbed, the negative potential charge barrier may be first diminished, neutralized, or even reversed to have a positive charge. E. Elvegård[36] studied the effect of introducing active cations into thiosulfate fixing baths to speed up the reaction between the thiosulfate and the silver halide. If the diffusion of the thiosulfate ion is not a limiting factor, then the acceleration of the complexing action would result in shortening the time of fixation. Later, M. Abribat and J. Pouradier[37] noted: "The addition of certain ammonium salts which adsorb strongly on silver halide crystals produced, as was anticipated, a reduction in the time necessary to produce a solution of the silver halide." Guanidine thiosulfate (or the addition of a guanidine salt to a sodium thiosulfate bath) was patented (U.S. Patent 2,174,494) as a means to speed fixing. More concentrated fixing baths are possible, according to British Patent 548,000, if urea is present in sodium or guanidine thiosulfate fixing baths.

Ethylenediamine was generally more effective than ammonium chloride in speeding fixation. Ammonium chloride had an optimum concentration beyond which the time of fixation increased. The accelerating action of these cationic substances upon fixation diminished as the concentration of the thiosulfate ions increased, presumably because the increased number of thiosulfate ions helped reduce the force needed to reach the surface of the silver halide. Some of the results seemed to indicate that the limitation of the speed of fixation is due to the slow rate of penetration of the gelatin layer (diffusion) rather than the chemical reactions occurring at the crystal surface.

Compounds containing various positively charged metallic ions have been studied by L. G. Welliver[38] as possible fixing accelerators in acid-hardening sodium thiosulfate baths. Compounds containing aluminum,

boron, cadmium, cobalt, copper, gallium, gold, indium, lead, nickel, silver, or zinc were without any effect. However, thallium compounds, which have been recognized for some time as accelerators for developing or fixing, were only effective for emulsions containing silver iodide. Welliver reported that "The addition of small concentrations of thallium ion (100–400 mg/l) increase the fixing rate and extend the working life of either fresh or exhausted sodium thiosulfate fixers used to fix photographic emulsions containing silver iodide." However, the thallium was ineffective in fixing baths containing appreciable quantities of ammonium thiosulfate.

Thallium is approximately as toxic as arsenic, is easily absorbed through the human skin, and has a strong cumulative effect. Because of its extremely toxic nature, thallium should not be included in fixing baths for general use.

RAPID THIOSULFATE FIXING BATHS CONTAINING AMMONIUM ION

The presence of ammonium ion in thiosulfate fixing baths as a means to secure rapid fixation was recognized as early as 1866, when John Spiller[39] advocated the use of ammonia or ammonium carbonate to increase the rate of fixation. Spiller also prepared and demonstrated the effectiveness of ammonium thiosulfate, and these compounds were said to be more rapidly eliminated from the emulsion layer during washing after fixation. Ammonium thiosulfate was difficult to prepare free from impurities at that time, the crystals took up water from the air, and the compound was much more costly than the sodium salt.

One means to obtain ammonium thiosulfate in solution, without starting out with the compound, is to add ammonium chloride or ammonium sulfate to a sodium thiosulfate solution, resulting in the presence of both the ammonium and thiosulfate ions in the solution.[40] This indirect method was used for the commercial Rapid Fixing Salt introduced by Agfa in 1906 (British Patent 25,869). The proper proportions of sodium thiosulfate and ammonium chloride to form the most effective fixing bath became the subject of considerable research. The optimum quantity of ammonium chloride, according to A. and L. Lumière and A. Seyewetz,[41] was less than that required to form ammonium thiosulfate. An increase in the rate of fixation was found only when the concentration of sodium thiosulfate was below 40%. They also noted that the silver thiosulfates formed by such fixing baths were less stable than those formed in the sodium thiosulfate baths without the ammonium chloride.

R. B. Willcock[40] found that increasing the thiosulfate concentration required a decrease in the ammonium chloride concentration, but for a 40% sodium thiosulfate fixing solution "the addition of ammonium chloride,

in any quantity, small or large, has little or no effect on fixing time." He agreed with the earlier findings of J. I. Crabtree and H. Parker[42] that 25 g/liter of ammonium chloride produced the most rapid fixation when used in a 20% sodium thiosulfate solution. Willcock recommended an extra-rapid acid-fixing formula that included 200 g sodium thiosulfate, 25 g ammonium chloride, and 10 g potassium metabisulfite per liter of solution. The composition of a fixing bath buffered to pH 6.0 was composed of 250 g sodium thiosulfate, 25 g ammonium chloride, 20 g potassium metabisulfite, and 10 g sodium sulfite in a liter of water. The baths were found to decrease the fixing time from 40 to 50% with the most rapid types of bromoiodide emulsions.

A rapid acid hardening fixing bath containing ammonium chloride was introduced by J. I. Crabtree, L. E. Muehler, and H. D. Russell[43] in 1942 as Kodak F-7 fixing bath. This bath fixes much more rapidly than the F-5 or F-6 fixing baths and has a considerably greater fixing capacity.

Kodak Rapid Fixing Bath F-7

Water, about 125°F (50°C)	600 ml
Sodium thiosulfate pentahydrate	360.0 g
Ammonium chloride	50.0 g
Sodium sulfite, desiccated	15.0 g
Acetic acid, 28%	48.0 ml
Boric acid, crystals	7.5 g
Potassium alum	15.0 g
Cold water to make	1.0 liter

Use crystalline boric acid rather than powdered boric acid, which is slow to dissolve. Dissolve the ingredients in the order listed.

Kodak F-7 has essentially the hardening constituents of the Kodak F-5 formula contained in a 36% sodium thiosulfate solution with 5% ammonium chloride present. The time to clear most negative films was less than the F-5 fixing bath and the capacity of the bath was almost 50% greater. The photographic characteristics of the fixing bath were improved by the presence of the ammonium chloride, but this compound brought a complication: chlorides in acid solution attack and pit certain types of stainless steel, such as contained in tanks, trays, clips, hangers, and other processing equipment. Stainless steel of types 302 and 304 was attacked but type 316 was not.

The normal tendency of a sodium thiosulfate fixing bath (without ammonium chloride) to pit stainless steel was not increased when 6% ammonium sulfate was added to the solution. The film clearing times and the degree of

hardening of such a fixing bath were similar for (1) Kodak F-7 fixing bath and (2) Kodak F-7 with the 5% ammonium chloride replaced by 6% ammonium sulfate. This last fixing bath was called Kodak F-9 fixing bath.

Kodak Rapid Fixing Bath F-9

Water, about 125°F (50°C)	600 ml
Sodium thiosulfate pentahydrate	360.0 g
Ammonium sulfate	60.0 g
Sodium sulfite, desiccated	15.0 g
Acetic acid, 28%	48.0 ml
Boric acid, crystals	7.5 g
Potassium alum	15.0 g
Cold water to make	1.0 liter

Use crystalline boric acid rather than powdered boric acid, which is slow to dissolve. Dissolve the compounds in the order listed in the formula.

The F-9 rapid fixing bath may be prepared by adding the Kodak F-5a stock hardener solution to a stock solution containing sodium thiosulfate and ammonium sulfate.

Sodium Thiosulfate–Ammonium Sulfate Stock Solution

Water, about 125°F (50°C)	750 ml
Sodium thiosulfate pentahydrate	450.0 g
Ammonium sulfate	75.0 g
Water to make	1.0 liter

To prepare Kodak F-9 rapid fixing bath from the two stock solutions, add one part of the cool stock hardener solution Kodak F-5a slowly to four parts of the sodium thiosulfate–ammonium sulfate stock solution. Stir rapidly during the mixing of the two solutions.

The F-9 formulation fixed more rapidly than the Kodak F-5 and had greater useful fixing capacity for water-rinsed or stop-bath-treated film. However, L. E. Muehler and J. I. Crabtree,[44] who formulated the F-9 composition, had this warning: "*Caution*: With rapid fixing baths, do not prolong the fixing time for fine-grained film or plate emulsions or for any paper prints; otherwise, the image may have a tendency to bleach, especially at temperatures higher than 68°F (20°C). This caution is particularly important in the case of warm-tone papers."

RAPID FIXING BATHS MADE WITH AMMONIUM THIOSULFATE

When ammonium thiosulfate was finally prepared commercially in sufficient purity in the 1940s, this compound was used to prepare rapid fixing baths, often in liquid form. Ammonium thiosulfate, $(NH_4)_2S_2O_3$, crystallizes without water of crystallization as colorless plates or needlelike crystals. Its molecular weight is 148 compared to 248 for sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$. Six parts of ammonium thiosulfate are equivalent to 10 parts of sodium thiosulfate crystals. A 60% solution of ammonium thiosulfate is the common commerical form. This represents about the maximum concentration, because even the 60% solution may precipitate crystals in cool weather. The chemical reactions of ammonium thiosulfate are similar to those of the other soluble thiosulfates. Sulfurization will occur readily when a solution of ammonium thiosulfate is acidified in the absence of sulfite ion. (See Figure 6.)

Donald B. Alnutt[16] found that "The time of clearing, and consequently the time of fixation of an ammonium thiosulfate fixing bath, is approximately

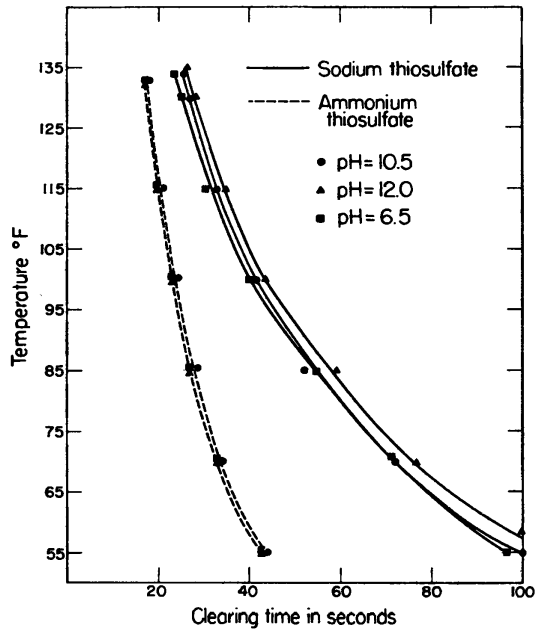


Figure 6. Less time is required at any temperature to clear Kodak Verichrome Pan film by ammonium thiosulfate than by sodium thiosulfate (0.25*M* solutions). The fixing action of the ammonium thiosulfate is particularly effective at the lower temperatures. [G. M. Haist, J. R. King, and L. H. Bassage, *Phot. Sci. and Eng.*, 5 (4): 199 (1961)]

one-fourth that of the common sodium thiosulfate baths." Fixing baths containing sodium thiosulfate and ammonium chloride were slower in their fixing action than baths made with the ammonium thiosulfate directly. Hardening fixing solutions containing ammonium thiosulfate retain satisfactory hardening action up to a pH of about 7; baths with sodium thiosulfate lose their hardening action at about pH 5.8, although the bath may still clear film. The capacity for hardening film is greater for the ammonium than for the sodium fixing solutions. Equal or greater efficiency may be obtained for a lower concentration of ammonium thiosulfate, making possible the formulation of concentrated liquid fixing solutions that require only dilution for use.

Ammonium thiosulfate fixing baths are relatively insensitive to increasing amounts of iodide up to certain limits. For modern bromoiodide films rapid fixing baths containing ammonium thiosulfate are more suitable than those that contain sodium thiosulfate, whose fixing times increase when small amounts of dissolved iodide build up in solution. It was reported by K. Frank[17] that more than 20 g of silver may be contained in a used ammonium thiosulfate fixing bath before the fixing time becomes too long. Such a quantity of silver would not be obtained in practice because of dilution of the bath. Solutions of ammonium thiosulfate become exhausted more by the dilution of the fixing bath than by increasing silver content.

Nearly exhausted ammonium thiosulfate fixing baths may deposit a precipitate of nearly colorless crystals, especially if the solution stands overnight as in automatic film processing machines. This crystal precipitate was noted by K. Frank[17] after processing film containing silver iodide. Other investigators[45,46] have reported that an ammonium argentothiosulfate bromide [nearest empirical formula: $(NH_4)_4(AgS_2O_3)_3Br$] is formed in a practical fixing bath when a silver bromide emulsion is fixed. This complex salt will contain some iodide when a bromoiodide emulsion is treated in an ammonium thiosulfate fixing bath. Because of its low solubility, this salt may form in the emulsion layer as well as in the solution. A high bromide and iodide content of the emulsion and a high degree of exhaustion of the fixing solution favor the formation of the poorly soluble salt. Under these conditions, the clearing time for the film would involve the time taken to dissolve the silver halide of the emulsion plus the time to solubilize any of the precipitated salt in the gelatin layer.

Formulas for Ammonium Thiosulfate Fixing Baths

A number of ammonium thiosulfate fixing baths have been formulated by Donald B. Alnutt.[16] Formula ATF-1 utilizes aluminum chloride as the

hardening agent. Both (1) a ready-to-use and (2) a concentrated version were compounded.

ATF-1:
Ammonium Thiosulfate General Purpose Acid-Hardening Fixing Bath

	Ready-to-Use	Concentrated
Water	700 ml	
Ammonium thiosulfate, 60% solution	185 ml	185 ml
Sodium sulfite, anhydrous	12 g	12 g
Acetic acid, glacial	9 ml	9 ml
Boric acid	7.5 g	7.5 g
Water to make	—	250 ml
Aluminum chloride hexahydrate	12.5 g	12.5 g
Water to make	1.0 liter	25 ml

Dissolve the chemicals in the order given.
Add the glacial acetic acid slowly while stirring.
Dissolve the boric acid in a small amount of hot water before adding.
When making the concentrated formula, keep the aluminum chloride solution separate from the ammonium thiosulfate solution. The ready-to-use fixing bath is made by adding 750 ml of water to the ammonium thiosulfate solution and then adding, while stirring, the ammonium chloride solution.

The ATF-2 fixing bath has rapid hardening action, being effective in the time necessary for the film to clear. However, like most chrome alum acid-hardening fixing baths, the bath has a short life and poor keeping properties.

ATF-2:
Ammonium Thiosulfate–Chrome Alum Acid-Hardening Fixing Bath

Water	700 ml
Ammonium thiosulfate, 60% solution	185 ml
Sodium sulfite, anhydrous	15 g
Sulfuric acid, 5% solution	80 ml
Potassium chrome alum	15 g
Water to make	1 liter

Dissolve the chemicals in the order given.

The 5% sulfuric acid solution can be made by adding 5 ml of the concentrated acid to 95 ml of cold water slowly with rapid stirring.

Potassium alum is a more conventional hardening agent when ultrarapid hardening action is not necessary. Fixing-bath formula ATF-5 containing potassium alum had an exceptionally long service life and hardened satisfactorily over a long period of time. The aluminum chloride in the ATF-1 bath produced the best hardening, but the hardening given by the ATF-1 was about equal to that given by the F-5 acid-hardening fixing bath.

ATF-5:
Ammonium Thiosulfate General-Purpose Acid-Hardening Fixing Bath

Water	700 ml
Ammonium thiosulfate, anhydrous	200 g
Sodium sulfite, anhydrous	15 g
Acetic acid, 28% solution	55 ml
Boric acid	7.5 g
Potassium alum	15 g
Water to make	1 liter

Dissolve the chemicals in the order given.

Dissolve the boric acid in a small volume of hot water before adding to the bulk of the solution.

The loss of silver image during fixation is directly proportional to the acidity of the bath.[14] Ammonium thiosulfate fixing baths have greater reducing action than sodium thiosulfate baths at the same pH. Films or plates should not be allowed to remain in ammonium thiosulfate baths more than twice the time to clear. Photographic paper prints are especially susceptible to the destruction of their finely divided silver image. No noticeable reduction of a silver image of a photographic film was observed by Alnutt during a 10-min immersion in ammonium thiosulfate fixing baths containing 150 g/liter of the thiosulfate salt. With baths containing 200 g/liter, such as ATF-5, however, marked image reduction was noticed after 8 min immersion. Prints fixed in this or similar ammonium thiosulfate rapid fixing baths should not be immersed in the solution for more than 4 minutes.

Concentrated ammonium thiosulfate fixers are often packaged in two parts: (1) a liquid hardener with an aluminum salt and (2) the fixing solution containing the ammonium thiosulfate. When the concentrated solution of thiosulfate is stored under tropical or other high-temperature conditions, the solution becomes cloudy and precipitates crystalline sulfur. (This action

will also occur in sodium thiosulfate concentrated solutions.) It was concluded by G. I. P. Levenson[47] that the sulfite reacted with the thiosulfate and, when all the sulfite was consumed, the sulfur from the thiosulfate was precipitated in the acid solution.

The autoxidation of sulfite, catalyzed by thiosulfate, was said to occur by a series of reactions.[48]

(1) $$4SO_2 + 3H_2O \longrightarrow 2H_2SO_4 + H_2S_2O_3$$

(2) $$H_2S_2O_3 \longrightarrow S + SO_2 + H_2O$$

Net reaction:

(3) $$3H_2S_2O_3 \longrightarrow 4S + 2H_2SO_4 + H_2O$$

However, C. J. Battaglia and W. J. Miller[29] have postulated the formation of a bisulfite-thiosulfate complex ion, $SO_2 \cdot S_2O_3^{2-}$, which reacts further to form ions containing decreasing amounts of sulfur (pentathionates, $S_5O_6^{2-}$; tetrathionates, $S_4O_6^{2-}$, and trithionates, $S_3O_6^{2-}$). Regardless of the exact mechanism of the reaction, the practical result is the destruction of the sulfite and the formation of sulfur from the thiosulfuric acid from the acid solution. Alnutt found that his highly acid ATF-2 bath sulfurized rapidly at 40°C (104°F), the ATF-1 solution precipitated sulfur in one week, and ATF-5, F-5, and F-7 remained free from turbidity for four weeks.

FIXING AGENTS OTHER THAN THIOSULFATES

A fixing agent should have at least the following properties: complex all the silver halides with sufficient rapidity throughout the useful life of the bath; not stain or attack the gelatin, the silver image, or the operator; form water-soluble silver complexes; and be low in cost, without odor, and nontoxic. The precipitation of insoluble silver compounds, especially during the washing step, or the precipitation of sulfur from the fixing agent itself, should not occur in acid, neutral, or alkaline solution.

The ideal fixing agent for darkroom and machine use should not harm the emulsion layer or the user of the solution, and the inexpensive agent should rapidly give water-soluble, stable silver complexes throughout the useful life of the solution. Unfortunately, as yet, the ideal silver complexing agent has not been found. In addition, modern requirements for fixing baths have changed considerably since 1933, when the standard acid-hardening thio-

sulfate bath with boric acid was compounded. Most of today's applications increase the demands made on silver complexing agents of the fixing solution. Even boron compounds may have to be eliminated because of their pollution potential.

High-temperature processing is becoming more common, both to reduce the time before the image may be evaluated as well as to increase the capacity of existing processing machines. Silver thiosulfates may be very unstable at temperatures about 100°F. This deposition of silver is very pronounced if the simplification of processing involves a combined developer-and-fixing bath (a monobath) where silver can be reduced from a thiosulfate complex in a few seconds. In other cases it is desired not to wash the fixed film or paper, thus saving time but reducing the permanence of the photographic image. With in-camera processing, washing is not possible and overcoating the instant print is not a desirable operation. These and other modern photographic applications increase the need for stable, stain-free, and rapid-acting fixing agents, causing a reevaluation of the well-known silver solvents and a search for silver complexing agents with properties superior to those of the thiosulfates.

Silver ions are extremely reactive, and thus a considerable number of compounds might be potential silver complexing agents for fixing solutions. The inorganic compounds usually contain nitrogen, sulfur, selenium, phosphorus, arsenic, or halide atoms. Organic compounds containing unsaturated linkages between carbon atoms, or loosely held hydrogen atoms because of nearby electron-attracting groups, or organic acids, are sufficient to combine with silver ions. But most common organic compounds that are useful for silver complexing contain the same atoms as the inorganic compounds, especially sulfur or nitrogen in a variety of configurations.

Compounds that interact with silver ions may be classified into four groups: singly charged negative ions; doubly charged negative ions; ammonia and organic amines; and other organic compounds. Reliable, comparative information of the practical effectiveness of the various nonthiosulfate silver-solubilizing agents is difficult to secure and relate to today's needs. Many of the compounds previously tested have been found to be unsuitable because of their degrading action upon gelatin. However, as gelatins are modified chemically or replaced by nongelatin substitutes, either partially or totally, then some of the characteristics of these fixing agents may prove to be more satisfactory. For temporary unwashed photographic prints, the fixing agent need not necessarily have to clear the photographic emulsion, only render it insensitive to the further effects of light. And as photographic processing becomes more mechanized and is less practiced by untrained individuals, the processing solutions may contain more toxic compounds (for example, the developing agents in color developers).

Singly Charged Negative Ions

Halide

Silver halides have very low solubility in water but do produce ions to an extremely small extent. F. F. Renwick[49] said that silver bromide required nearly 10 million times and silver iodide from 500 to 1000 million times its weight in water to dissolve. The introduction of a small concentration of a halide ion results first in a decrease in solubility of the silver halide, causing the ionic solubility to reach a minimum. Then the solubility of the silver halide increases because of the formation of complex ions between the introduced halide and the silver halide. In the presence of the added halide ions the total solubility of the silver halide is the sum of the solubility caused by the formation of complex ions and the ionic solubility. Increasing amounts of halide ions produce increased amounts of complex ions and hence increased solubility of the silver halide. It was noted by T. H. James[50] that with 0.001 *M* potassium bromide present, the complex solubility of the silver bromide equals the ionic solubility; at 0.01 *M* potassium bromide the complex solubility is 1000 times greater; and at 0.1 *M* potassium bromide the complex solubility is 100,000 times greater than the ionic solubility.

Chloride ions solubilize silver chloride by forming $AgCl_2^-$, $AgCl_4^{3-}$, and Ag_2Cl^+ complex ions, but the chloride ions have little effect on either silver bromide or silver iodide. Magnesium chloride as well as common salt (sodium chloride) has been used as a source of the chloride ions. Bromide ions solubilize either silver chloride or silver bromide through the formation of complex ions $AgBr_3^{2-}$, $AgBr_5^{4-}$, Ag_2Br^+, $AgCl_3Br^{3-}$, or $AgClBr_3^{3-}$. Iodide ions, which attract silver ions much more strongly than either bromide or chloride because of the low solubility of the iodide complexes, form complex ions AgI_2^-, AgI_4^{3-}, or Ag_3I^{2+}. Renwick[49] found that 100 ml of a 30% solution of potassium iodide would dissolve about 3 g of silver iodide, forming the double salts, AgI·KI and AgI·2KI. A 1% solution of potassium iodide completely converted the silver bromide to iodide in a few minutes at room temperature. However, Renwick noted, "Such a fixing bath (30% solution of potassium iodide) suffers from the serious drawback that it causes softening or even melting of the gelatine film, unless the latter has been well hardened first." Rudolf Fisher patented (German Patent 681,737) a 25% potassium iodide solution containing formaldehyde as a rapid fixing bath. Concentrated potassium bromide solutions also attack and degrade the gelatin of the emulsion layer.

To prevent the attack of concentrated halide solutions upon gelatin, Pierre Glafkides[51] suggested the presence of a hardening agent in the solution.

Water	1000 ml
Potassium bromide	350 g
Potassium alum	10 g

Fixing time was 12 min, producing the double salt, $AgBr \cdot KBr$, with silver bromide.

Concentrated solutions of potassium iodide dissolve silver chloride and silver iodide four times more rapidly than silver bromide. A two-solution hardening iodide formulation was suggested by Glafkides.[51]

Solution A

Water	1000 ml
Potassium iodide	200 g

Solution B

Water	1000 ml
Potassium alum	100 g
Acetic acid	3 ml

Five parts of A are combined with one part of B. The fixing time is 5 to 10 min for silver iodide.

Cyanide

Potassium cyanide has a very great affinity for silver ions and is capable of dissolving even the most insoluble of silver compounds, such as silver iodide or silver sulfide. Double cyanides, $AgCN \cdot KCN$, are formed and the gelatin is strongly attacked. A study by Merle Randall and J. O. Halford[52] has been made of the solubility of precipitated silver iodide in potassium cyanide, as given by the equation

$$AgI\ (ppt) + 2CN^- \longrightarrow Ag(CN)_2^- + I^-$$

James lists three possible silver complexes of increasing cyanide content, $Ag(CN)_2^-$, $Ag(CN)_3^{2-}$, and $Ag(CN)_4^{3-}$.

Potassium cyanide is much too poisonous for almost all practical purposes, and the use of this compound for photographic processing is to be avoided.

Thiocyanates

Ammonium thiocyanate, NH_4CNS, was suggested as a fixing agent by M. Meynier[53] as long ago as 1863. Unlike sodium thiosulfate, ammonium thiocyanate did not precipitate sulfur under the influence of acids. In 1875 G. Hooper[54] said "That sulphocyanide of silver is formed by the immersion of the toned prints is the *primary* action, and that a double salt formed through the excess of sulphocyanide of ammonium is the *secondary* action, and that a certain small amount of sulphocyanide of silver (which is insoluble in water) may ultimately remain in the prints is the *final* result."

Pierre Glafkides[51] reported that potassium thiocyanate, KCNS, dissolved only silver chloride and bromide well, forming double salts.

$$AgBr + 2KCNS \longrightarrow AgCNS \cdot KCNS + KBr$$

A hardening agent should be present in thiocyanate solutions to avoid the excessive softening of the gelatin produced by such solutions. Solution of the gelatin was found to be gradual for 10% ammonium thiocyanate solutions but very rapid for strengths above 10%.[55] Photographic films or papers for use with thiocyanate solutions are usually highly hardened in manufacture.

The following thiocyanate fixing solution was suggested by Glafkides.[51]

Water	1000 ml
Potassium thiocyanate	50 g
Potassium alum	10 g

Fixing time was 2 to 5 min, to be followed by a rinse of the photographic material in a fresh bath of the same composition. Although the emulsion layer will clear quickly, a water-insoluble opaque silver salt may be precipitated when the emulsion layer is treated with water. A sufficient treatment in the fresh thiocyanate bath will avoid the precipitation of a double salt in the gelatin layer.

The reactions

$$AgCl\,(s) + CNS^- \longrightarrow AgCNS\,(s) + Cl^-$$

$$AgBr\,(s) + CNS^- \longrightarrow AgCNS\,(s) + Br^-$$

showing the conversion of solid silver halide into a solid silver thiocyanate were given by Merle Randall and J. O. Halford.[52] T. H. James[50] listed three possible complexes: $Ag(SCN)_2^-$, $Ag(SCN)_3^{2-}$, and $Ag(SCN)_4^{3-}$. It has been

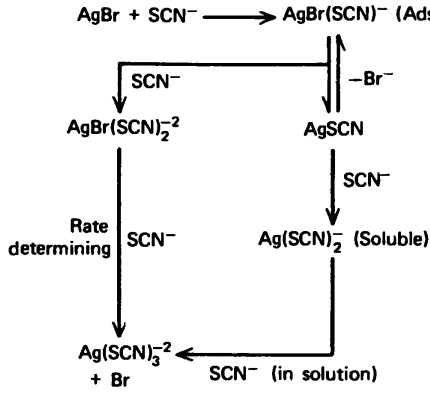


Figure 7. Reaction scheme for the conversion of silver bromide to soluble silver thiocyanate complexes. [M. R. V. Sahyun, *Phot. Sci. and Eng.*, 17: 176 (1973).]

reported that 9.77 g/liter of aqueous potassium thiocyanate at 25°C will dissolve 19.10 mg/liter of silver bromide precipitate.[56] (See Figure 7.)

In 1914 C. Welborne Piper[57] tested aluminum, sodium, potassium, and ammonium thiocyanates (called sulphocyanides then) and said, "The quickest rate is shown by ammonium sulphocyanide, which at 35 per cent takes 15 seconds only, or about one-fifth the time of ammonium thiosulfate at its quickest." The difficulty of having insoluble thiocyanates formed in the gelatin layer caused Piper to suggest that

> a mixture of hypo and ammonium sulphocyanide should give a rapid fixing bath free from the disadvantages of sulphocyanide alone, if this compound is added only in small quantities. Tests show that the most rapid combination must contain 30 per cent of hypo, or the same concentration as is necessary to give the best results with ammonia. If to this strength of hypo we add $2\frac{1}{2}$ per cent of ammonium sulphocyanide the time of fixing is reduced to 43 per cent, while 5 per cent of sulphocyanide reduces it to 35 per cent. Greater quantities effect greater reductions, and by increasing the sulphocyanide to 30 per cent we can reduce the time to one-fifth. In view, however, of the action of the sulphocyanide on gelatin 5 per cent may be regarded as the maximum that can be used with safety, and $2\frac{1}{2}$ per cent gives a very useful reduction of time.

A bath consisting of 30% sodium thiosulfate and $2\frac{1}{2}$% ammonium thiocyanate in water was said to fix in two-thirds the time of 40% sodium thiosulfate alone. Today, the combination of thiocyanate and thiosulfate is often used for the rapid fixation of photographic materials, particularly for those applications where rapid access to the image is more important than the

long-time keeping characteristics of the image. A patented composition[58] for hardened microfilm had the following composition:

Sodium thiosulfate, crystals	280 g
Ammonium thiocyanate	140 g
Potassium sulfite	80 g
Water to make	1 liter

Fixing time was 10 sec at 80°F. Both the ammonium thiocyanate and the potassium sulfite help to solubilize or decolorize the antihalation dye layer located between the film base and the emulsion layers of the photographic film. The absence of hardening agents in the fixing bath permits archival washing to occur in the shortest possible time.

Doubly Charged Negative Ions

Thiosulfates

The most widely used and economical silver complexing agents are the thiosulfates, whose practical use in fixing baths has already been described. However, ever since thiosulfate began to be the fixing agent for silver halide–gelatin photographic materials, concern has been voiced about the stability of the silver image, both during fixing and even after washing and drying. Robert H. Bow[59] expressed this concern in 1887 when he said, "To the usual mode of fixing photographic prints by means of hyposulphite of soda there are two leading objections: the first is the thorough after washing required, necessitating the expenditure of much time and water to get rid of the hyposulphite of soda and silver; the second is the doubt that overshadows the process as to the permanency of the prints even after all this trouble. To eliminate this second objection, various oxidizing agents have been proposed, such as peroxide of hydrogen, chlorine, etc., to destroy the last traces of the hyposulphites; but these are, I believe, seldom employed. At any rate, the first objection is so formidable as to make it desirable to escape from it."

Sodium Sulfite

This compound, common to both developers and fixing baths, is a weak solvent for silver chloride and, to a lesser extent, for silver bromide. In 1887 W. de W. Abney[60] recommended two baths of sodium sulfite for fixing paper prints. Randall and Halford[52] list the complexing reactions as

$$AgCl + 2SO_3^{2-} \longrightarrow Ag(SO_3)_2^{3-} + Cl^-$$

$$AgBr + 2SO_3^{2-} \longrightarrow Ag(SO_3)_2^{3-} + Br^-$$

T. H. James[50] lists the possibility of a weak complex, $AgSO_3^-$, and two more stable ones, $Ag(SO_3)_2^{3-}$, and $Ag(SO_3)_3^{5-}$. The solubility of precipitated silver bromide in aqueous solutions of sodium sulfite and potassium bromide has been studied when 25 g/liter of sodium carbonate was also present in the solution.[56] The presence of the carbonate did not have any appreciable effect on the solubility of the silver bromide in the sulfite and/or bromide solution.

As shown in Table 1, from the work of M. A. Hill, C. W. Zuehlke, and A. E. Ballard,[56] the presence of potassium bromide required a greater concentration of the sulfite to achieve the same silver bromide solubilization. For example, 25 g/liter of sodium sulfite was sufficient to solubilize 0.400 g of silver bromide, but in the presence of only 0.57 g of potassium bromide the concentration of the sulfite had to be raised to 40 g/liter in order to solubilize the 0.400 g of silver bromide.

Ammonia and Organic Amines

Ammonia, NH_3, is a gas, but the water solution of the gas, NH_4OH (ammonium hydroxide), is capable of solubilizing considerable quantities of silver chloride, less of silver bromide, and very little silver iodide, unless in very concentrated solution. Ammonium carbonate, $(NH_4)_2CO_3$, has been used to replace ammonium hydroxide. Robert H. Bow[59] in 1887 reported that a 2% solution of ammonia dissolved a weight of silver chloride equal to 50% of the ammonia present and that a 7% solution dissolved a weight of silver chloride equal to two-thirds of the ammonia present. When aqueous ammonia is added to silver chloride, a silver-ammonia complex is formed[52] according to

$$AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2^+ + Cl^- + 2H_2O$$

The advantages of ammonia fixation included (1) freedom from the use of a sulfur-containing compound that may impair image permanency, (2) a great saving in water for washing because the ammonia complex, $Ag(NH_3)_2^+$, is readily water-soluble, and (3) less loss of fine image detail in the alkaline ammonia fixing solution. Disadvantages arise because ammonia is a volatile gas with a pungent odor. Inhalation of the concentrated gas may cause death. Ammonia escapes from its solutions, especially at high altitudes or if the solution temperature rises considerably, making it difficult to maintain a solution of known strength. Ammonium hydroxide, containing 28 to 29% ammonia in water, is strongly alkaline with a pungent odor because of the escape of the ammonia gas.

Organic compounds of ammonia, called the amines, are capable of dissolving silver halides much in the fashion of the aqueous solution of ammonia. Methyl amine, ethanolamine, triethanolamine, diethylaminoethanol, and

Table 1. Equivalent Solvents for AgBr at 25°C

Observed AgBr Solubility (g/liter)	Solvent Composition (g/liter)		Observed AgBr Solubility (g/liter)	Solvent Composition (g/liter)	
	KBr	Na_2SO_3		KBr	Na_2SO_3
0.020	0	1.2	0.400	0	25.0
	2.00	8.0		0.57	40.0
	5.00	16.5		1.56	60.0
	6.7	20.0		2.00	67.2
	10.0	23.5		3.42	80.0
0.050	0	3.2	0.500	0	31.0
	2.00	15.0		0.30	40.0
	2.00	16.5		1.14	60.0
	5.00	31.5		2.00	74.2
	10.00	41.0		2.50	80.0
0.100	0	6.2	0.600	0	37.2
	1.10	20.0		0.09	40.0
	2.00	27.5		0.81	60.0
	3.60	40.0		1.88	80.0
	5.00	46.2		2.00	81.2
	10.00	59.5	0.700	0	43.3
	10.6	60.0		0.56	60.0
0.200	0	12.6		1.40	80.0
	0.40	20.0	0.800	0	49.1
	1.57	40.0		0.34	60.0
	2.00	45.0		1.06	80.0
	4.05	60.0	0.900	0	54.7
	5.00	64.8		0.16	60.0
	9.45	80.0		0.77	80.0
	10.0	81.0	1.00	0	60.2
0.300	0	18.8		0.54	80.0
	0.10	20.0			
	0.96	40.0			
	2.00	56.9			
	2.27	60.0			
	5.00	80.0			

ethylenediamine are only a few examples of the organic amines that exert some solvency for silver chloride and silver bromide. Often organic amines may be used in conjunction with other weak silver solvents to provide a satisfactory level of silver complexing action required in a specific photographic process.

Organic Silver Complexing Compounds

Many organic compounds can interact with silver ions, but for film clearing to occur, the silver complex must be water-soluble. Double- and triple-bonded carbon compounds have some attraction for silver ions, but in most cases the compounds have low solubility unless solubilizing groups are present. Organic compounds containing sulfur in the form of $-\overset{|}{\underset{|}{C}}-SH$, $\diagdown C{=}S$, and $-\overset{|}{\underset{|}{C}}-S-\overset{|}{\underset{|}{C}}-$ combine readily with silver ions but only clear the emulsion layer when the silver compound has sufficient solubility to diffuse from the gelatin layer. The presence of one or more acidic groups, such as carboxyl (—COOH) or sulfonic acid ($-SO_3H$), helps to confer sufficient solubility in alkaline solution. Sugar groups, such as pentose or hexose residues, provide important solubilizing functions. For solubility in acid solution, as well as under alkaline conditions, amino groups ($-NH_2$), imino groups (=NH), or ring nitrogens $\left(-\overset{|}{\underset{H}{N}}- \text{ or } =N-\right)$ often provide solubility for the silver ion–organic compound. In many cases both carboxyl and amino groups are found in the same molecule of efficient film-clearing agents. And as the water solubility of the organic compound increases, there is less likelihood of the strong sulfurous odors that are often characteristic of organic sulfur compounds. Organic silver complexing agents based on sugars are often free of any odor.

Thiosinamine or allyl thiourea, $NH_2-\overset{S}{\overset{\|}{C}}-NH-CH_2-CH{=}CH_2$, was suggested in 1893 for fixing silver chloride materials.[61] According to Pierre Glafkides, a slightly acid 1% solution was capable of dissolving silver chloride in 5 min. Later in the same year A. Bogisch[62] pointed out that thiourea, $NH_2-\overset{S}{\overset{\|}{C}}-NH_2$, should be restricted in use as a fixing agent because some insoluble compounds of thiourea and silver may be precipitated in the gelatin of the emulsion layer. Complete elimination of these

compounds by washing in water was not possible. In addition, the thiourea attacked and softened the gelatin of the emulsion layer.

The complexing action of thiourea with silver ions has been the subject of considerable investigation. Three common complexes have been reported:

$$\left[Ag\left(NH_2C(=S)-NH_2\right)\right]^+, \left[Ag\left(NH_2C(=S)-NH_2\right)_2\right]^+,$$

and

$$\left[Ag\left(NH_2C(=S)-NH_2\right)_3\right]^+.$$

The 1:1 complex is sparingly soluble but dissolves in excess of either silver ions or thiourea. A polymeric form, $\left[Ag_2\left(NH_2C(=S)-NH_2\right)_3\right]^{2+}$, has been reported that has each sulfur bonded to two silver atoms. The same bonding has been said to occur in the 1:3 silver:thiourea complex. This polymeric structure accounts for the low solubility of the thiourea complexes. Thiourea-silver complexes that are low in thiourea are unstable, resulting in the formation of Ag_2S.[63]

Thiourea has found specialized use as a silver complexing agent. Although thiourea will fog film in more than mildly alkaline solution, it has been used in developers or monobaths of pH less than about 10.5. The clearing curve of a fine-grained bromoiodide film by thiourea has been given by G. M. Haist, J. R. King, and L. H. Bassage.[25] The effect of temperature was considerable, the film clearing time dropping from 100 sec at 55°F to 19 sec at 130°F. Other thioureas, such as ethylene thiourea and methyl- or ethyl-substituted thioureas, have also been used as silver complexing agents.

Mercapto Acids

The mercapto acids are effective film-clearing agents but usually only under alkaline conditions, such as in a monobath or an alkaline fixing bath. However, mercaptosuccinic acid was used as a fixing agent in highly acidic titanium monobaths in 1956 by Grant Haist et al.[64] In 1961 mercaptoacetic acid (sometimes called thioglycolic acid), cysteine hydrochloride, and *o*-mercaptobenzoic acid were found to be film-clearing agents only in alkaline solution. Cysteine—that is, mercaptopropionic acid with an amino group in the molecule—was the most efficient at pH 10.5, especially at a temperature of 130°F where the time to clear was 15 sec for a fine-grain bromoiodide film.[25] (See Figure 8.)

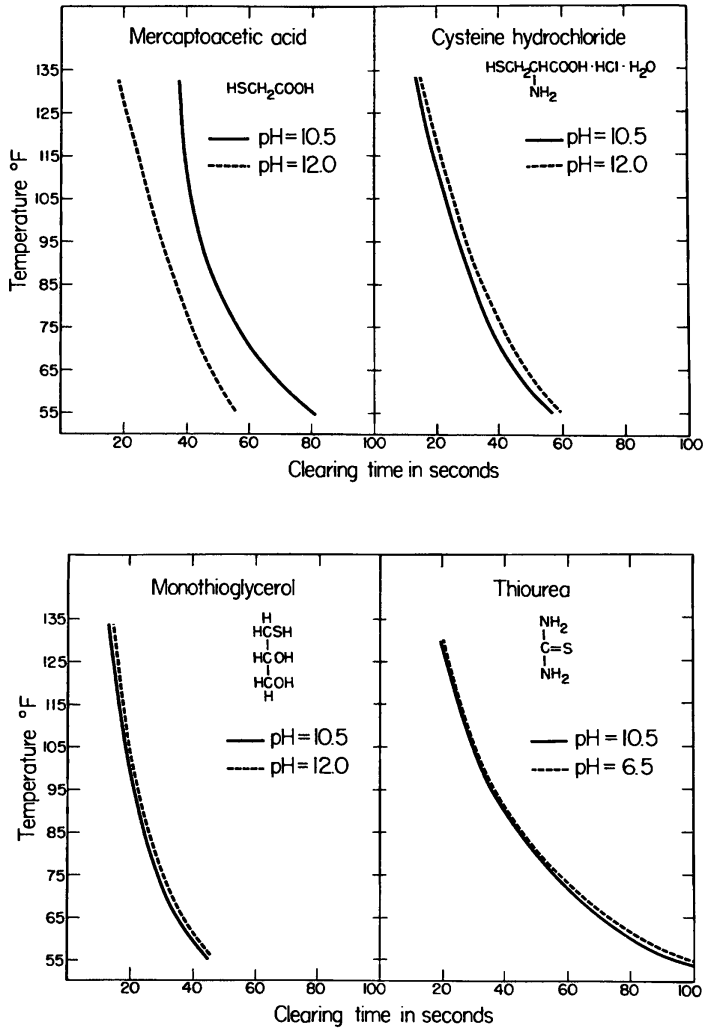


Figure 8. Most organic silver complexing agents require alkaline conditions in order to clear photographic film. Some compounds, however, such as thiourea or *N,N*-diethylaminoethanethiol, are effective under acidic conditions as well. [G. M. Haist, J. R. King, and L. H. Bassage, *Phot. Sci. and Eng.*, 5 (4): 199–200 (1961).]

A comparison of the speed of fixing of silver bromide by thiosulfate and mercapto acids has been made recently.[65] The following order of film clearing was determined: sodium thiosulfate < ammonium thiosulfate < mercaptoacetic acid < mercaptosuccinic acid < cysteine. Low concentrations of mercapto acids gave rapid film clearing, with cysteine being the most effective of all the compounds tried. Some mercapto compounds, such as mercaptoacetic acid, are toxic and have a bad odor, but cysteine is an odorless amino acid that may be utilized by the human body. Generally, the speed of film clearing by mercapto acids increased with the concentration of the compound, with the alkalinity of the solution, and with the temperature of the solution for a given degree of solution agitation.

The mechanism of fixing with mercapto acids has been investigated by T. N. Gerasimova and A. V. Bromberg.[66] According to these investigators, "These observations suggest that silver halide is fixed in two stages. At first a certain relatively difficultly soluble compound or silver complex is formed with thiol in the emulsion layer at the diffusion front of the fixing agent, where its concentration is small. Then the complex reacts with fresh supplies of the fixing agent, which arrive because of diffusion. As a result of this additional reaction, a new silver compound is formed with the thiol. This is easily soluble."

Five mercapto acids—cysteine, mercaptoacetic, thiosalicyclic, mercaptosuccinic acid, and a compound called Unithiol (2,3-dimercapto-1-propanol sodium sulfonate, $CH_2(SH)CH(SH)CH(OH)SO_3Na$)—were found to act in a similar fashion. The poorly soluble silver mercaptide formed first contained silver:mercapto acid in a 3:2 proportion. When the proportions reached 1:1—that is, $Ag^+/RS^- = 1$—easily soluble complexes were formed. This overall reaction for the 1:1 silver complex formation may be written, using mercaptoacetic acid,

$$AgBr + HSCH_2COOH \longrightarrow AgSCH_2COOH + HBr$$

Many of the mercapto acids form silver complexes much more stable than the silver thiosulfates, suggesting the use of these mercapto compounds for highly alkaline solutions or for processing at high temperatures. However, certain organic sulfur compounds hold silver as loosely as does the thiosulfate, so that they may be used for processes such as diffusion transfer, where the silver ions must be transferred from the photosensitive material to suitable deposition sites. Therefore, organic compounds may be selected or prepared to suit any possible requirement of a photographic process.

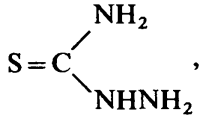
2-Mercaptopyrimidines can serve as high-speed fixing agents in an alkaline solution.[67] Stop baths after development were said to be unnecessary, as development was "instantaneously stopped" when the silver halide emulsion

was immersed in the alkaline solution of the 2-mercaptopyrimidines. In addition, the silver complexes formed were so readily soluble that only a short rinse in water was sufficient to remove them. Fixing times were more rapid than with an ammonium thiosulfate solution. An alkaline solution of 4-amino-6-hydroxy-2-mercaptopyrimidine (pH = 13.6), containing 0.3 mole of the compound per liter, fixed a film emulsion in 15 sec as compared with the 40 sec necessary with a 0.3 mole/liter solution of ammonium thiosulfate (pH = 5.9). An alkaline 30% solution of the disodium salt of 2-mercapto-4-hydroxy-6-aminopyrimidine (pH = 13) may be added to a developer, such as Agfa Rodinal (1:100), to stop development and fix the film. Only 2.5 ml of the pyrimidine solution was needed for each 100 ml of the developer.

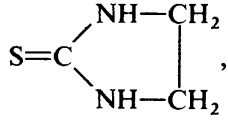
Thiosemicarbazones and thiocarbohydrazones have been proposed by Grant Haist and W. J. Humphlett[68] as silver halide solvents for a number of photographic processes. Film clearing time for dihydroxyacetone thiosemicarbazone was 46 sec in 5% acetic acid and 5% sodium acetate, 55 sec in water, and 40 sec in 5% sodium carbonate. The effective pH range of the thiosemicarbazones was said to extend from pH 4 to about pH 11.5.

Chemical Additions to Thiosulfate Fixing Baths

Thiosemicarbazide,



or 2-imidazolidinethione,



have been patented[69] as ingredients of ammonium thiosulfate fixing baths suitable for use after developing solutions that contain high concentrations of potassium ions. Because of the greater solubility of potassium salts, potassium compounds (potassium carbonate, potassium hydroxide, potassium bromide) are often present in concentrated liquid developers. The carryover of potassium ions in a light-sensitive material, however, slows fixation with an ammonium thiosulfate fixing bath because of the formation of the less-soluble potassium thiosulfate. The addition of thiosemicarbazide

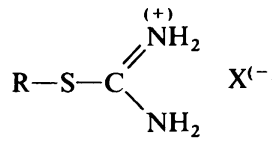
or 2-imidazolidinethione in the fixing bath was claimed to alleviate this loss of fixing rate. An example of such a formulation is

Ammonium thiosulfate	150 g
Sodium sulfite monohydrate	15 g
Sodium metaborate	15 g
Glacial acetic acid	15 ml
Potassium alum	20 g
Thiosemicarbazide	9 g
Water to make	1 liter

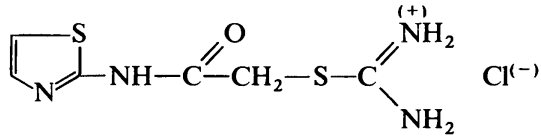
Polyethyleneglycols have been claimed[70] to increase the fixing rate and capacity of thiosulfate fixing baths. Two grams of Carbowax 1540 (Union Carbide and Carbon Chemicals) in a liter of thiosulfate fixing solution decreased the film clearing time and increased the capacity of the solution.

Silver halide emulsions, particularly those partly or entirely of chloride, may produce silver images that change color when heated during ferrotyping. The finer the silver image, the greater is the chance that the black silver image may become brown or greenish-brown. This bronzing of the silver image is often called plumming. Antiplumming compounds are usually incorporated in the emulsion layer during manufacture, but such compounds have been added to photographic solutions, including the fixing bath. For use in the fixing bath, Edith Weyde[71] patented substances "which form difficultly soluble silver salts and are transformed only very slowly into soluble complex compounds with the aid of thiosulfate, that is to say, which more difficultly form a soluble complex compound with sodium thiosulfate than silver chloride or silver bromide. The substances which enter into consideration behave in the fixing bath in the same manner as behaves a small quantity of iodine which yields with silver and thiosulfate more difficultly soluble complex compounds than the chloride or bromide. Probably the difficultly soluble complex compounds form a protective layer around the silver particles and thus protect them against the slight dissolving property of the fixing bath and against aggregation." Examples of such image-protecting compounds included lysalbinic acid, cystine, thiosemicarbazide, guanylthiourea, thiohydantoin, thiobenzamide, thiobarbituric acid, and other organic sulfur compounds. Two grams of lysalbinic acid were added to a liter of fixing bath, but only 0.1 g/liter was needed of a compound such as 4-ethylthiochlorobenzoic acid.

Antiplumming agents represented by the formula



(where R is an alkyl group and X is a halogen atom) may be added to fixing baths, according to Edward B. Knott and John Morgan.[72] Five grams of



S-2-thiazylamidomethyl thiuronium chloride

in a liter of fixing bath was claimed to insure "very deep blacks" after ferrotyping of the silver image. S-Ethylthiuronium bromide, S-*n*-butylthiuronium bromide, and S-amidoethylthiuronium chloride were also proposed as antiplumming compounds.

FIXATION OF NONGELATIN EMULSION LAYERS

Gelatin has been universally used as a protective colloid or carrier for silver halide crystals. Current practice may use small amounts of nongelatin substances to replace some of the gelatin in the carrier. This substitution may cause some change in the rate of fixation, but the major change occurs when almost all the gelatin has been replaced by a polymeric substance, such as polyvinyl alcohol or a cellulose ester. These polymeric resins are not readily permeated by conventional fixing baths. Several fixing solutions suitable for treating nongelatin silver halide layers have been patented by John I. Crabtree and George T. Eaton:

1. Alcohol (methyl, ethyl, or butyl)-water-thiourea.[73]
2. Alcohol (methyl, ethyl, or butyl)-water-thiocyanate (sodium, potassium, or ammonium).[73]
3. Aqueous solution of sodium thiocyanate and thiourea.[74]
4. Aqueous solution of iodide (sodium, potassium, or ammonium) and thiocyanate (sodium, potassium, or ammonium).[75]
5. Aqueous solution of iodide (sodium, potassium, or ammonium) and thiourea.[75]
6. Inorganic thiocyanate and ethanolamine, such as 100 g sodium thiocyanate and 100 ml ethanolamine added to a liter of 30% sodium thiosulfate.[76]

SILVER RECOVERY

Photographic materials consume more than 50 million troy ounces of silver per year—about one-third of the total silver used by industry. On the average, about 75% of the silver contained in black-and-white photographic film products is dissolved by the processing solutions, mostly in the fixing bath.[77] The remaining 25% of the coated silver constitutes the negative image. With black-and-white photographic printing papers, up to 90% of the silver may be removed from the final print.[78] Essentially all of the coated silver of color films and papers is removed, leaving only the dye image in the photographic material. This almost complete removal of the silver from color products prompted M. L. Schrieber[79] to comment that the film manufacturer gives you the color image but only lends you the silver.

The amount of potentially recoverable silver is significantly influenced by the type of photographic material, the processing method and equipment used, the degree of exhaustion of the processing solution, and the relative efficiency of the method of silver recovery. Current manufacturing practices may lower the amount of silver available in photographic products. The silver content of equivalent products by different manufacturers may vary considerably. One photographic manufacturer[80] has attempted, however, to estimate the silver that is potentially available for recovery after processing various films or papers (see Table 2). (One gram of silver per liter of solution equals 0.12169 troy ounce of silver per gallon of solution.)[81]

Most of the potentially recoverable silver is found in fixing baths, particularly those used for silver-rich X-ray films. An estimate of the typical silver content of used fixing baths has been made by R. O. Dannenberg and G. M. Potter.[89] Ammonium thiosulfate fixing baths, when well used, contain more silver than sodium thiosulfate fixing baths. (See Table 3.)

In black-and-white reversal processing the silver of the original negative image is solubilized in the bleach bath, where the greatest share of the silver is to be found. The dichromate bleach converts the metallic silver to soluble silver sulfate.

$$6Ag + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Ag_2SO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

Well-used bleach baths may contain only about 1 g silver per liter of bleach solution, however, because the baths' limited life does not allow the buildup of silver. With continuous processing, a high replenishment rate keeps the quantity of silver in the bleach solution at a fairly low level.

Silver recovery has not been universally practiced in the past except at large commerical motion picture and photofinishing laboratories. The

Table 2. Quantity of Silver Potentially Available for Recovery from Appropriate Processing Solutions

Product Processed	Units	Troy Ounces/ 1000 Units
	Photofinishing Films and Papers	
Color negative films	1-620 or 1-135/36 roll	9.5 to 10.5
Color reversal films	1-620 or 1-135/36 roll	6.5 to 7.5
Black-and-white negative films	1-620 or 1-135/36 roll	3.5 to 5.0
Color prints from negatives	$3\frac{1}{2} \times 5\frac{1}{2}$-in. print	0.35 to 0.45
Reversal color prints	$3\frac{1}{2} \times 5\frac{1}{2}$-in. print	0.35 to 0.45
Black-and-white prints from negatives	$3\frac{1}{2} \times 5\frac{1}{2}$-in. print	0.20 to 0.30
	Commercial and Professional Films and Papers	
Color negative films	8 × 10-in. sheet	11.0 to 12.5
Color reversal films	8 × 10-in. sheet	10.5 to 11.5
Black-and-white negative films	8 × 10-in. sheet	4.5 to 6.0
Color prints from negatives	8 × 10-in. sheet	0.4 to 0.5
Black-and-white prints from negatives	8 × 10-in. sheet	1.0 to 2.0
Stabilization papers	1 sq ft	1.5 to 2.5
	Motion Picture Films	
Color negative films	1 ft × 35 mm	2.0 to 2.5
Color print films	1 ft × 35 mm	0.8 to 0.9
Black-and-white negative films	1 ft × 35 mm	1.2 to 1.8
Black-and-white print films	1 ft × 35 mm	0.8 to 1.0
Black-and-white reversal films[a]	1 ft × 16 mm	0.3 to 0.4
Color reversal films	1 ft × 16 mm	0.75 to 1.0
	Radiography Films	
Medical X-ray films (screen type)	14 × 17-in. sheet	20 to 30
Industrial X-ray films	14 × 17-in. sheet	65 to 85
	Graphic Arts Films	
Lith-type films (50% exposure)	8 × 10-in. sheet	3.5 to 5.5
Continuous-tone films	8 × 10-in. sheet	4.5 to 6.0
Stabilization papers	1 sq ft	1.5 to 2.5

Table 2. ***(continued)***

Product Processed	Units	Troy Ounces/ 1000 Units
	Aerial films	
Camera negative films	1 ft × 9½-in. wide	5.5 to 8.0
Duplicating films	1 ft × 9½-in. wide	2.5 to 6.5
	Instrumentation Films and Papers	
Recording films	1 sq ft	8.0 to 12.0
Recording papers, stabilization-processed	1 sq ft	1.5 to 4.5
	Drawing Reproduction Products	
AUTOPOSITIVE films	20 × 24-in. sheet	25 to 50
AUTOPOSITIVE papers	20 × 24-in. sheet	25 to 30
	Business Systems Products	
Microfilms	1 ft × 16 mm	0.20 to 0.30
Photocopy papers, standard negative	1 sq ft	2.0 to 2.5

Source: "Recovering Silver from Photographic Materials," Eastman Kodak Co., 1969.[80]

[a] Silver is recoverable from the bleach by precipitation with sodium chloride.

economics of silver recovery from smaller installations and individual users has been unfavorable because of the low cost of both the silver and the thiosulfate. Recently, silver consumption has outpaced production and the metal has risen in price. In addition to salvaging a scarce metal of considerable value, silver recovery has other potential benefits. Electrolytic recovery systems rejuvenate the fixing bath so that it may be reused. Continuous removal of silver permits the fixing bath to operate more uniformly and consistently throughout its useful life. Maintaining the silver content of the fixing bath at a low level provides better image stability, because the excess of thiosulfate ions insures the formation of the more stable and water-soluble complexes of silver. If fixing baths can have their useful life lengthened, fewer solutions need be made, stored, or discharged into sewers to pollute the environment.

Table 3. Composition of Various Spent Photographic Fixing Baths

Type of Solution	Composition, g/liter							
	Ag	Na_2O	K_2O	Al_2O_3	NH_4	COOH	$S_2O_3^{2-}$	SO_3^{2-}
Aerial print fixer	0.65	21.8	0.7	0.9	—	6.0	33.9	2.16
X-ray fixer	10.1	14.6	3.1	2.8	31.9	28.0	91.4	8.8
Black-and-white print fixer	1.0	(a)	(a)	0.2	—	1.5	66.6	13.0
Black-and-white film fixer	5.6	(a)	(a)	1.8	—	67.0	121.0	9.1
Color print fixer	1.56	(a)	(a)	0.9	—	(a)	24.3	13.5
Color film fixer	3.76	(a)	(a)	0.2	—	1.0	91.8	8.4

(a) No data.

Silver Recovery Methods

Recovery of silver from a fixing bath involves removal of the silver from the silver thiosulfate complex, usually by precipitation of the silver. Common methods of silver recovery involve precipitation by forming a silver compound that is less soluble than the silver thiosulfate complex; precipitation by chemical reduction of the silver complex; precipitation by displacing the silver from the thiosulfate complex by another metal ion; precipitation of the silver from the complex by using electrolytic cells that cause the silver to be deposited as a silver plate on the negatively charged electrode of the cell; and separation of the silver by ion-exchange beds.

Precipitation by Formation of Silver Sulfide

Adding sodium sulfide, $Na_2S \cdot 9H_2O$, or potassium sulfide, $K_2S \cdot 5H_2O$, to a fixing bath causes the precipitation of sulfide sludge that is 40 to 70% silver.[82] Because silver sulfide is one of the most insoluble of all silver compounds, the sulfide precipitation method is one of the most efficient, requiring only settlement tanks and little technical knowledge.

$$Na_2S + Na_4Ag_2(S_2O_3)_3 \longrightarrow Ag_2S + 3Na_2S_2O_3$$

Sodium sulfide is commonly used as the precipitant, since it is a much cheaper source of sulfur than the potassium salt. The addition of sodium sulfide to an acid fixing bath will liberate hydrogen sulfide, H_2S, a poisonous gas with a very objectionable odor. Contact of this gas with photographic materials will cause fog, so silver recovery with sodium sulfide should not be attempted from acid fixing baths in darkroom or other areas containing sensitized photographic products.

To prevent this liberation of the hydrogen sulfide gas, the fixing bath must be made alkaline first before the sodium sulfide is added. An automatic system using spent developer and sodium sulfide was developed by K. Hickman and D. Hyndman,[83] but the method of J. I. Crabtree and J. F. Ross[82] has been the one most widely used when 100 or more gallons of used fixer are available weekly. The used fixing bath is placed in a nonmetal container and made alkaline by adding 30 ml of a sodium hydroxide solution per gallon of the fixing bath. (The sodium hydroxide solution is made by dissolving, slowly and with stirring, 900 g of the sodium hydroxide in four liters of cold water.) If the fixing solution does not turn litmus paper blue or give an alkaline indication by any other method, more sodium hydroxide should be added until the solution gives an alkaline reaction. Then add 1.5 ml of the sodium hydroxide to each liter of solution to insure distinct alkalinity.

The sodium sulfide solution is made by dissolving 900 g sodium sulfide in four liters of hot water. Thirty milliliters of this sulfide solution is added for each four liters of the fixing bath that has been made alkaline. A brownish-black precipitate settles. When the solution above the precipitate is clear, test a small portion of the clear liquid by adding a small volume of the sulfide solution. If a precipitate forms in this test solution, indicating incomplete precipitation of the silver from the fixing bath, more silver sulfide must be added until the test solution yields a clear solution. Then allow the solution to stand overnight, drain off the clear liquid, separate the sludge, and either dry in the sun or oven, or pack in a watertight container.

Silver recovery methods using sulfide precipitation of silver are usually unpleasant because of the odor of the sulfide. In addition, the waste solution contains a high concentration of thiosulfate ions. Disposal of this waste solution may be a pollution problem because of the high oxygen demand of the thiosulfate ions. A recovery method of alkaline chlorination, proposed by Thomas N. Hendrickson and Thomas J. Dagon,[84] destroys the thiosulfate ions, generating sulfur or sulfide ions for the precipitation of the silver from solution. The chlorine is thought to cause a localized acidity that decomposes the thiosulfate.

$$\underset{\text{chlorine}}{Cl_2} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{hypochlorite ion}}{OCl^-} + \underset{\text{hydrogen ions}}{2H^+} + \underset{\text{chloride ion}}{Cl^-}$$

$$\underset{\text{hydrogen ion}}{H^+} + \underset{\text{thiosulfate ion}}{S_2O_3^{2-}} \longrightarrow \underset{\text{bisulfite ion}}{HSO_3^-} + \underset{\text{sulfur}}{S}$$

$$\underset{\text{sulfur}}{S} + \underset{\text{silver}}{2Ag} \longrightarrow \underset{\text{silver sulfide (precipitate)}}{Ag_2S\downarrow}$$

Another reaction may involve

$$\underset{\text{sulfite ions}}{4SO_3^{2-}} \longrightarrow \underset{\text{sulfide ion}}{S^{2-}} + \underset{\text{sulfate ions}}{3SO_4^{2-}}$$

$$\underset{\text{sulfide ion}}{S^{2-}} + \underset{\text{silver ions}}{2Ag^+} \longrightarrow \underset{\text{silver sulfide (precipitate)}}{Ag_2S\downarrow}$$

The overall reaction is thought to be represented by the equation

$$\underset{\text{thiosulfate ion}}{S_2O_3^{2-}} + \underset{\text{hydroxyl ions}}{10OH^-} + \underset{\text{chlorine}}{4Cl_2} \longrightarrow \underset{\text{sulfate ions}}{2SO_4^{2-}} + \underset{\text{water}}{5HOH} + \underset{\text{chloride ions}}{8Cl^-}$$

The reaction requires a considerable number of hydroxyl ions and the solution must be alkaline. Introducing chlorine gas into a sodium hydroxide solution forms sodium hypochlorite, so that a commercially prepared hypochlorite solution may be used in place of the chlorine gas. One liter of spent fixing bath may be combined with half a liter of 15% sodium hypochlorite (by weight) to form a pH 11 mixture that precipitates silver sulfide within a few minutes.

Precipitation by Chemical Reduction with Sodium Hydrosulfite

The silver ion may be extracted from the thiosulfate complex and reduced to silver by either a developing agent or a strong nonselective reducing agent. Adding 12 oz of a discarded developer to 8 oz of the exhausted fixing bath, then 1 oz of 10% sodium hydroxide, was proposed by Philip A. Friedell[85] as a method to precipitate silver without sulfur in about 24 hr. Strong reducing agents, such as sodium hydrosulfite, $Na_2S_2O_4$, or sodium borohydride, $NaBH_4$, have been suggested for silver recovery. Sodium hydrosulfite, proposed by A. Steigmann[86] in 1921, really should be called sodium hyposulfite, but this name has mistakenly become associated with sodium thiosulfate in common use.

According to Steigmann, sodium hydrosulfite precipitates silver by the following equation.

$$2NaAgS_2O_3 + Na_2S_2O_4 \longrightarrow 2Ag + 2Na_2S_2O_3 + 2SO_2$$

Later, J. B. Firth and J. Higson[87] analyzed the precipitate obtained from the use of sodium hydrosulfite in fixing baths. They found sodium sulfide as part of the residue, which they proposed was formed in the following reaction.

$$2NaAgS_2O_3 + Na_2S_2O_4 \longrightarrow Ag_2S + Na_2S_4O_6 + Na_2SO_4$$

Both reactions are thought to occur, yielding a very compact, black sludge of silver and silver sulfide with a content of about 85% silver.

Steigmann[86] gave these directions for silver recovery with sodium hydrosulfite: "For one liter of well-exhausted fixing bath 6–8 g. hydrosulfite and just as much sodium carbonate is used. An average of 4–5 g. pure silver is obtained. The precipitation is almost quantitative."

The bath may be allowed to stand 1 to 2 days to insure precipitation of the silver and silver sulfide, or the solution may be heated to 50 to 60°C, which will cause the precipitation of the silver to occur much more rapidly. Heating not only speeds the deposition of the silver but also destroys the excess of the hydrosulfite. Steigmann claimed that "the fixing bath was ready for use immediately after filtering," and could be recovered three times by this method. The fixing bath, however, has been made alkaline with sodium

carbonate to prevent the formation of unpleasant gases that might be liberated by the formation of the sulfurous acid. The carbonate need not be added if 30 g sodium sulfite is used with 30 g sodium hydrosulfite for each four liters of fixing bath. Even so, the availability, purity and cost of sodium hydrosulfite have limited the application of this method of silver recovery.

Precipitation by Displacement of the Silver by Other Metals

Silver is considered a noble metal because it is more difficult to dissolve than other metals, such as copper, iron, and zinc, which are referred to as base metals. When a solution of a silver salt is brought in contact with one of the base metals, the base metal goes into solution to replace the silver and the silver is precipitated from solution. This well-known method of refining silver can be adapted for silver recovery. The addition of scraps of brass, copper, zinc, or steel to a used fixing bath causes displacement of the silver from the thiosulfate complex. The silver is either deposited upon the surface of the metal or falls to the bottom of the container. Unlike chemical precipitation by sulfide or hydrosulfite, there is no mixing and storing of chemical solutions, and little attention is needed during the precipitation of the silver.

1. *Precipitation by zinc.* Addition of zinc to an exhausted fixing bath precipitates silver without the liberation of harmful or disagreeable gases.[88]

$$Na_4Ag_2(S_2O_3)_3 + Zn \longrightarrow 2Ag + ZnS_2O_3 + 2Na_2S_2O_3$$

The metallic zinc may be in the form of dust, granules, shavings, or sheet. The dust has the greatest surface area, giving a higher rate of silver precipitation than by the other forms of zinc. Silver recovery with zinc should be carried out in a nonmetal container. For best results the fixing bath should be acid, as it usually is. If the exhausted bath is not acid, add glacial acetic acid until just acid, such as might be indicated with the red color of red litmus paper. Adding 15 ml more of glacial acid for each four liters of fixing bath will insure the distinct acidity needed. Five grams of zinc dust for each liter of solution is added with vigorous stirring and the solution allowed to stand overnight.

Usually, 16 to 24 hr is sufficient for complete precipitation of the silver. The completeness of the precipitation may be roughly estimated by immersing a piece of bright copper wire or strip in a small volume of the clear solution. If, after one minute, the copper does not have a silvery coating, the precipitation of the silver from the fixing bath may be assumed to be complete. The sludge from an acid bath contains silver (mostly as the sulfide), zinc metal, zinc oxide, and sodium thiosulfate. The probable silver content was estimated by Crabtree and Ross to fall between 15 to 40% silver for the dried sludge.

The quantity, purity, and division of the zinc influence the rate of precipitation. Silver was precipitated more quickly from an acid solution, but complete precipitation could be obtained from an alkaline solution that was allowed to stand overnight. Stirring the solution greatly accelerated the precipitation. Crabtree and Ross state, "In the case of the zinc dust method, the silver could be completely precipitated in from 15 to 30 minutes, if the solution was constantly stirred, but if the solution was allowed to stand without agitation several hours were required for complete silver precipitation at ordinary room temperatures." These investigators found "that at a temperature of 50 to 60°C (120 to 140°F) the silver could be completely precipitated from an exhausted fixing bath almost immediately, if twice the theoretical quantity of zinc dust was used in acid solution."

2. *Precipitation by copper and brass.* Precipitation by zinc yields a sediment that contains considerable zinc and only a moderate amount of silver. The use of copper and brass sheet is a slow method of silver recovery, but the deposited silver is almost pure. The technique is described by Helmut Gernsheim[78]: "A long strip of polished copper sheet is placed in the residue at an angle, so that both sides are presented to the liquid, and left there for about three days. When taken out it should be rinsed; the black precipitate is then removed with a knife and washed off into a container for metallic silver. This thin coat is difficult to remove, so it may be left until the next batch of residues is to be treated. Then a strip of thin brass sheet (about 1 mm in thickness) is placed in the former solution and allowed to remain for another 48 hours. Thus practically the last trace of silver will be extracted and the fluid can be poured away. The whitish silver precipitate should be rinsed, and the silver will flake off if the brass is bent sharply two or three times."

3. *Precipitation by iron.* Different forms of iron, zinc, and copper may be used to precipitate the silver from an exhausted fixing bath. Using a standard hypo solution that had been tagged with radioactive $Ag^{110}NO_3$, R. O. Dannenberg and G. M. Potter[89] studied the silver precipitation rate to the specific area of a considerable number of metallic precipitants. As shown in Table 4, these investigators found that the precipitation rate is directly proportional to the specific surface area, and that there was no significant difference in the rate at which the silver was precipitated by different metals. Dezincked window screen and steel wool, both inexpensive and readily available, were efficient collectors of silver from the fixing solution.

A silver recovery system based on metal displacement would be affected by the solution flow rate, the flow continuity, the silver concentration in the fixing solution, the acidity of the fixing solution, and the thiosulfate concentration of the solution as well as the type of precipitant, its coarseness, and

Table 4. Silver Precipitation Rate

Precipitant	Specific Surface Area, cm^2/g	Precipitation Rate	
		%/min	%/min/cm^2
Shingle nail	2.25	0.71	0.32
Carpet tack	2.8	1.14	0.41
18-gauge wire, iron	5.7	1.47	0.26
Tin can	6.0	1.47	0.25
Wire nail	6.2	2.08	0.34
Wire staples	10.8	5.00	0.46
Galvanized window screen	18.5	5.90	0.32
Dezincked window screen	19.9	7.10	0.36
Grade 00 steel wool	120.0	>50.0	0.41
Zinc sheet	3.2	1.46	0.46
Zinc sheet	5.4	1.84	0.34
Zinc wire, 0.01-in.-diam.	21.4	7.7	0.36
Copper sheet	8.9	2.2	0.25

the packing density (of steel wool units). These factors were studied by Dannenberg and Potter, who reported

a. No significant difference between grades 0 and 1 steel wool (specific surface area of 120 and 100 cm^2/g), but slightly more silver was deposited on the coarser grade 2 steel wool (50 cm^2/g).
b. A looser packing of the steel wool increased the precipitating capacity of the steel wool, but the slight increase would not justify a larger container for a recovery unit.
c. Column diameters of 1.75 and 4.00 in. packed with steel wool precipitated almost the same amount of silver per gram of steel wool.
d. Almost twice as much silver was precipitated by each gram of window screen as by an equal amount of zinc shavings, and steel wool had a better precipitating capacity than the zinc. (Doubling the life of the fixing bath has been claimed for the use of aluminum wool.[90])
e. Steel wool precipitated 50% of the silver from the standard fixing bath in 1 min with an efficiency of over 99% at all flow rates up to one liter/min for a 1.75 × 12-in. recovery column. Window screen required at least 10 times longer in contact with the solution to achieve an efficient rate of precipitation.

f. Increasing the idleness period of a recovery unit reduced the precipitating capacity and the quality of the sludge because of the increased oxidation of the iron.
g. The precipitation capacity of steel wool increased significantly with increasing silver concentration in the fixing solution. The steel wool was consumed four times faster for a 1-g/liter silver solution than for a 10-g/liter solution.
h. Steel wool did not precipitate silver from a pH 11 solution, indicating that the displacement reaction will proceed only if the solution will corrode the metal precipitant. Increasing solution acidity will increase iron consumption per unit weight of silver precipitated.
i. Increasing the thiosulfate concentration of the fixing solution did reduce the amount of silver precipitated per gram of steel wool, but the variation was not significant.

When iron displaces silver from the silver thiosulfate complexes of an exhausted fixing bath, the solution becomes charged with iron salts and must be discarded. According to Dannenberg and Potter, the iron is introduced by two reactions:

1. Acid dissolution by the acetic acid of the solution:

$$2CH_3COOH + Fe \longrightarrow (CH_3COO)_2Fe + H_2$$

2. Displacement of the silver ion:

$$Ag_2S_2O_3 + Fe \longrightarrow FeS_2O_3 + 2Ag$$

In theory, one atom of iron replaces two atoms of silver, but the practical efficiency is less than this. Some of the iron is lost when it dissolves in the acid solution and cannot then take part in the displacement reaction. Some steel wool remains unconverted when the recovery operation must be ended because the silver complexes begin to pass through the unit. A utilization efficiency of 60% was estimated by G. I. P. Levenson,[91] so that 10 lb of steel wool should collect 23 lb of silver. A commercial steel wool collector, the Kodak chemical recovery cartridge, claims to remove up to 99% of the available silver. Two such cartridges may be connected in series to insure maximum silver recovery when flow rates are high.[92] A description of a cartridge-type recovery unit is given by Harlan Glenn Hartman[93] in British Patent 1,093,810.

Simple steel wool recovery units made from inexpensive, readily available materials will efficiently precipitate silver from intermittent batches of exhausted fixing solution, such as might be obtained from limited darkroom operations. Proper construction of such a unit requires that the exhausted

solution enter the recovery unit at the bottom and overflow at the top; once wetted, the steel wool must never be exposed to the air during the lifetime of the unit (rusted steel wool is ineffective for the displacement reaction to precipitate silver); and the steel wool should not be allowed to touch the metallic surface of a container, as serious corrosion will occur. Units constructed of plastic, glass, or other nonmetals are preferred, but a metal container may be protected with a chemical-resistant surface coating. Large industrial recovery units, described by G. I. P. Levenson or R. O. Dannenberg and G. M. Potter, are essentially scaled-up versions of simple steel wool units. When properly constructed and with a suitable retention time of the solution in the unit, silver recovery with steel wool is, according to Levenson,[91] "second to none in cheapness and efficiency."

The construction of a simple unit for small-scale operation has been described by Dannenberg and Potter:[89]

> Materials required are (1) a quart jar, (2) a plastic tee and nipple, (3) a funnel with a stem large enough to fit snugly in the tee, (4) a small cork to fit tightly in the throat of the funnel, and (5) steel wool packing. The plastic tee with nipple is inserted into the jar with the tee on the bottom and the end of the nipple level with the top of the jar. Steel wool is packed tightly around the nipple and tee. A small V-slot should be cut into the side of the cork to allow solution to flow at the rate of approximately 0.5 pint per minute.
>
> To operate the unit, the funnel with the cork flow regulator is fitted in the pipe nipple, the unit is placed in a sink, and spent hypo is poured into the funnel. Solution is allowed to overflow the jar and drain to waste. After the available solution has passed through the unit, the funnel is removed, the jar is closed with a lid, washed off, and placed in storage until another batch of solution becomes available.

The silver content of sludge from steel wool recovery units may range from 27% silver for a low-grade sludge to over 80% for high-quality sludge. Generally, it is advisable to save the sludge until a considerable amount has accumulated before shipping to a silver reclaimer. This is true with any silver recovery method, as it minimizes the costs imposed by the reclaimer, which may be considerable. A nationwide list of silver reclaimers is given in Kodak Publication J-10.[80] Dannenberg and Potter list how-to-do-it procedures for both reduction and oxidation smelting to produce at least 990 fine silver. Both of these procedures, however, require a chemical treatment of the sludge in a crucible heated to 1250°C for 1 hr.

Silver Precipitation by Electrolysis

When an electric current is passed between two uncorrodible electrodes immersed in a water solution of a silver salt, such as silver nitrate, the silver

metal is deposited at the negative electrode (the cathode) and oxygen gas is evolved at the positive electrode (the anode). Theoretically, a flow of 1 A of electrical current for 1 hr between the electrodes deposits 4 g of metallic silver on the cathode. In practice, only about 3 g of silver are deposited.[96] When a moderate electric current is applied through inert electrodes immersed in an aqueous solution containing silver thiosulfate, such as an exhausted fixing bath, oxygen is not liberated at the anode, and a black precipitate of silver sulfide is formed near the cathode. The suspension of the silver sulfide turns the solution black and contaminates the electrodes.

Electrolytic silver recovery must prevent the formation of the silver sulfide and promote the deposition of metallic silver at the cathode. Difficulties are encountered because the silver in a fixing bath exists in two forms: (1) a few positively charged silver ions, resulting from the dissociation of complex silver ions

$$AgS_2O_3^- \longrightarrow Ag^+ + S_2O_3^{2-}$$

and (2) a great number of silver complexes, such as $Ag(S_2O_3)^-$, $Ag(S_2O_3)_2^{3-}$, and $Ag(S_2O_3)_3^{5-}$, which are negatively charged. In an electrolytic cell, the electricity supplies the electrons at the cathode, so the silver ion is reduced there.

$$Ag^+ + 1\,e \longrightarrow Ag\ (\text{metal})$$

Most of the silver in the exhausted fixing bath is in the form of the negatively charged complexes which are attracted toward the positive electrode, the anode. Only a few silver ions are available at the cathode, but an excess of electrons is available. Under these conditions the more abundant thiosulfate ion is attracted to the cathode, where it is reduced.

$$S_2O_3^{2-} + 2e \longrightarrow SO_3^{2-} + S^{2-}$$

The sulfide ion then reacts immediately with the few available silver ions to form the insoluble silver sulfide.

$$2Ag^+ + S^{2-} \longrightarrow Ag_2S\ (\text{precipitate})$$

If the silver thiosulfate complexes can be kept from migrating away from the anode, the following reactions occur, according to Duisenberg.[97]

$$2Na^+ + AgS_2O_3^- \longrightarrow Na_2S_2O_3 + Ag^+$$

$$Ag^+ + 1e \longrightarrow Ag\ (\text{metal})$$

Silver deposition at the cathode is the result of this secondary reaction. Migration of the thiosulfate complexes of silver must be prevented in order to

maintain the concentration of silver ions near the cathode. The removal of soluble ion products formed at the cathode would also be advantageous.

1. *Factors controlling the efficiency of electrolytic units.* (a) *Agitation.* Maintaining a sufficient silver-ion concentration at the cathode will minimize sulfide formation. Hickman and his co-workers[98,99] found that critical adjustment of conditions (vigorous agitation of an acid, sulfite-containing fixing bath) could yield a plating efficiency as high as 80% in very large installations using a high current density for the electrolysis. An inter-electrode paddle wheel system was used to sweep the surface layer of solution away from the cathode and supply solution containing silver thiosulfate complexes. Air agitation[100] and rotating electrodes have been proposed as an alternative to provide a lesser but satisfactory degree of agitation.

(b) *Silver content of the solution.* The more silver ions near the cathode, the higher is the permissible current density without causing sulfiding. The higher the flow of current, the more silver can be deposited on the cathode. At current densities of 1 A/sq ft Hickman was able to remove almost all of the silver from the exhausted fixing bath. With an acid sodium thiosulfate fixing bath containing more than 6 g silver per liter of solution, a current density of 8 A could be used to plate out the silver and still not cause sulfide precipitation. For such high current densities, however, extremely vigorous agitation was required.

Low-current, low-agitation methods of electrolytic silver recovery were patented by Henri Georges Doffin[101] in 1937. Doffin found that a critical decomposition voltage existed such that at voltages between 0.20 and 0.40 V/sq ft a good silver plate without sulfiding was obtained even without agitation or with baths having low silver concentrations. This finding made possible simple recovery units consisting of a stainless steel cathode and carbon or graphite anodes that could be suspended in the fixing bath while a low current was passed. The Purhypo System[102] (Pennellier Co., Ltd., London, England) and the Baker recovery unit (Baker-Platinium Ltd., Birmingham, England) are commercial units of this type. A graphite anode and a wire screen mesh cathode, operated at 1.0 to 1.2 V dc, has been patented for electrolytic silver recovery.[103]

Low current density of a silver recovery unit means limited deposition of silver, unless many units are used or the units have very large surface areas. At a current density of 20 mA/sq ft A. A. Rasch and J. I. Crabtree[104] estimated that it would require $2\frac{1}{2}$ sq ft of cathode area for 1 hr to recover the silver from one 8 × 10-in. sheet of film. Somewhat higher current densities may be used, but the quality of the silver plate is reduced. Intermittent electrolytic silver recovery from the processing solution in use, dependent upon the passage of

the photographic material, has been claimed to have high reliability and a high yield of pure silver.[105]

(c) *Type of fixing bath.* Higher current densities are possible with ammonium thiosulfate fixing baths than with sodium thiosulfate baths, allowing the plating of more silver from the ammonium thiosulfate baths. Better silver plates are obtained from acid solutions, especially with pH near 4.5, than from alkaline fixing solutions. Acid condition of an exhausted fixing bath is often assured by adding acetic acid to the bath before silver recovery is attempted.

(d) *Sulfite concentration of the fixing bath.* Excess sodium sulfite in the fixing bath is necessary to insure good silver plating under any conditions. The reduction of the thiosulfate ion at the cathode produces sulfide and sulfite ions. An excess of sulfite in the solution causes the sulfite ion to combine with the sulfide ion to reform thiosulfate, thus avoiding silver sulfide precipitation. Sulfite concentration normally drops during electrolysis because of the anodic oxidation of the sulfite.

$$H_2O + SO_3^{2-} \longrightarrow SO_4^{2-} + 2H^+ + 2e$$

Failure to maintain a suitable sulfite concentration, depending on the silver concentration and the current density, will eventually cause sulfiding.

Rasch and Crabtree[104] state that

> In an acid fixing bath containing between 1 and 5 grams of silver per liter electrolyzed at normal current densities, good plating is obtained when the sulfite concentration (as sodium sulfite) exceeds 8 to 10 grams per liter. At lower sulfite concentrations, the plate deposited becomes increasingly brown in color. When sulfite concentration is of the order of 3 to 5 grams per liter, bad sulfiding of both the solution and the plate occurs. In some cases when the silver concentration was high, good plating was obtained even at these low sulfite concentrations. Little or no silver sulfide formed and, instead, elemental sulfur was precipitated in the bath. This was apparently due to an anodic reaction since the first traces of sulfur appeared in the solution around the anode. This would indicate that sulfite also acts as an inhibitor to certain anodic reactions.

Practical levels of sodium sulfite around 25 g/liter are to be preferred, as this concentration of the sulfite gives a better silver plate and avoids solution problems.

(e) *Gelatin concentration in the fixing bath.* Gelatin and gelatin degradation products were found by Hickman[106] to be deposited at the cathode, and the presence of these products promoted the formation of a smoother silver plate. Excess gelatin, however, is detrimental, because it forms a soft plate that traps solution and causes sulfiding to occur. The addition of 0.05 g thiourea

per liter of solution has been suggested as a means to improve plating from solutions containing excess gelatin.

(f) *Other factors affecting silver recovery.* Many other lesser factors influence the efficiency of electrolytic silver recovery. Dirt, coagulated gelatin, oil, or other impurities may contaminate the cathode, but suitable filtration can minimize this source of poor plating. The buildup of halide ions in the fixing solution has been reported to decrease the quality of the silver plate. The concentration of halide ions is not thought to reach a harmful level in systems using the low-current-density recovery units.

Accumulation of bromide and iodide ions in the desilvered fixing bath does decrease its fixing rate. Addition of a thallous salt precipitates all the iodide and most of the bromide ions. According to Karl Kieser,[107] a fixing bath may be restored to be equivalent of a freshly made bath. Thallous ions are poisonous, and precipitation methods require special attention. In a recent British patent,[108] the fixing bath was electrolyzed to recover the silver, and the solution was contacted "with polyethylene glycol or a derivative thereof which glycol or derivative has a polyethylene chain having a molecular weight of at least 400." The fixing solution may be circulated through a bag containing one or more polyethylene glycols. It was claimed that the fixing solution may be used repeatedly, markedly reducing the amount of fresh replenisher required.

2. *Galvanic silver recovery units.* When certain metals, such as zinc and copper, or zinc and stainless steel, are brought into electrical contact and placed in an exhausted fixing bath, a relatively high current flows between them. Zinc dissolves in the solution, and silver is plated on the copper or stainless steel electrode. The high current density soon depletes all the silver ions near the cathode, and the reduction of the thiosulfate ions begin to cloud the solution with silver sulfide.

Several small devices, which may be immersed in the fixing bath to increase the resistance of the circuit, have been marketed as silver recovery units, such as the Argeco unit (Collingridge and Co. Ltd., Watford, England).[109] Separating the electrodes by porous sheets, restricting solution flow, separating the electrodes but connecting them by insulated wire, are a few of the methods employed to make galvanic units less subject to sulfide precipitation. Even so, according to C. J. Sharpe,[110] sulfiding may occur in fixing baths low in silver, or silver may be precipitated in the solution in silver-rich fixing solutions.

The galvanic unit is a simple and compact but slow method of silver recovery of limited capacity. The amount of silver collected is equivalent to the zinc ions that go into solution. Thirty grams of zinc will yield 100 g of silver. Galvanic recovery units do require some care to avoid precipitation problems. A survey[111] of commercially available silver recovery units

indicates that there are many units of the more expensive agitated electrolytic models, but States Smelting and Refining Corp., Lima, Ohio, has low-cost galvanic units which, when returned, the manufacturer will replace, making payment for 50% of the silver collected.

Separation of Silver by Ion-Exchange Methods

Insoluble cation-exchange resins are high-molecular-weight polymeric substances that may contain phenolic, carboxylic, or sulfonic acid groups. When the hydrogen of the acid group is displaced, its place may be taken by a positively charged ion. Anionic exchange resins are insoluble high-molecular-weight polymeric substances which have basic groups of the amine, quaternary ammonium, or guanidinium type. Under acid conditions such a resin may bind negatively charged ions. The bound ions may often be liberated by flushing the resin bed with a concentrated solution of a strong electrolyte such as common salt (sodium chloride). Beds of anionic and cationic resins may be adapted for absorbing the positively charged silver ions and the negatively charged silver thiosulfate ions found in exhausted fixing baths. The limited capacity of some resins has limited this method to the removal of silver and other ions from wash water.[112,113]

The rejuvenation of photographic solutions by the ion-exchange process has been the subject of research at the Polytechnic Institute of Brooklyn.[114] The final report of this government-contracted work claims that "A process was developed for the rejuvenation of photographic fixing solutions. This process consisted in conditioning a bed of anion exchange resin with a solution of fresh fix, followed by passing a depleted fix solution through this bed. Substantially all of the silver and bromide was removed from the depleted fix, rejuvenating it completely."

Miscellaneous Methods of Silver Recovery

A hydrolyzed sugar solution obtained from wood was used by Eduard Farber[94] to precipitate silver from spent photographic solutions heated almost to the boiling point. The desired result is thought to be obtained through the action of several substances, probably the chemical reduction of the silver complex by the reducing sugars and an adsorption of the silver by high-molecular-weight compounds, such as lignin.

A 1950 British patent[95] claims

a process for recovering silver halide from a solution containing silver halide and organic matter, such as a waste solution containing silver halide together with gelatin

and produced in the manufacture of photographic light-sensitive materials, which process comprises subjecting the waste solution to an active sludge treatment to oxidize and decompose the organic matter in the solution aerobically, adsorbing the silver halide on the active sludges and precipitating the sludge together with silver halide, and then recovering the silver halide adsorbed on the active sludges and dissolved in the supernatant liquid.

By "active sludge" we mean herein a sludge collected from the bottom of a river and containing soil bacteria, which have been caused to multiply by storing the sludge for a period (e.g., about a month) whilst feeding them with a nitrogen- and phosphorous-rich medium.

The active-sludge process was designed primarily for recovering silver from the silver halide in the washing of photographic materials during manufacture. Another patented process (U.S. Patent 3,501,378) for this purpose involves the storage of the wash water for 10 to 20 hr in a container open to the air. Bacteria from the air decompose the gelatin in the water by fermentation. Then the silver halide is precipitated by aluminum sulfate (50 ppm).

The Reuse of Fixing Baths

The increase in silver concentration of a fixing bath is only one of a number of factors that slows the action of the solution. The wet film or paper entering the fixing bath may dilute, contaminate, or cause a reaction with the chemicals of the bath. Gelatin and halide ions accumulate in the solution. Sulfite and thiosulfate ions may be consumed and the acidity of the solution may be changed. When the photographic material leaves the bath, some of the essential ingredients, such as thiosulfate ion, may be carried out into the wash water.

Most silver recovery methods consider the exhausted fixing bath as a waste solution from which the silver is extracted before the solution is discarded. Only the electrolytic and ion-exchange methods permit an extension of the exhaustion life when dilution of the bath or carryout are not the major factors in the exhaustion. When the exhaustion is due primarily to the increasing concentration of silver in the bath, it was estimated by Rasch and Crabtree[104] that electrolytic silver recovery may permit possible chemical savings of approximately 20% for amateur and professional roll and sheet films fixed in ammonium thiosulfate fixing baths and approximately 40% for the same photographic products fixed in sodium thiosulfate baths. Chemical savings were estimated up to 400% for X-ray materials fixed in ammonium thiosulfate solutions and 200 to 500% for single-bath paper fixing systems.

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Chapter 14
Making the Image Permanent

The permanence of the silver image in processed film and paper is related to the degree of sulfiding of the silver in the image which takes place during fixation and the amount of silver thiosulfate complex and thiosulfate which remain after the washing process.

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Fixation consists of converting the water-insoluble silver halides of the emulsion layer into water-soluble silver thiosulfate complexes. Then, washing the photographic material in water removes most of the thiosulfate and silver thiosulfates by diffusion into the water. A lack of understanding of the need for complete fixing and washing has resulted in the loss of many of the negatives and prints made during the early years of photography. A silver photographic image that has been inadequately fixed or washed will, under the adverse storage conditions of high humidity and temperature, lose density and discolor, a condition called fading.

The reason for this change of the silver image upon storage is usually the partial or total conversion of the image silver to silver sulfide by (1) the attack from the sulfur contained in the residual thiosulfate or (2) the sulfur released from the decomposition of silver thiosulfate complexes that were not removed by washing in water. Decomposition of silver thiosulfate complexes also produces silver sulfide, which discolors the clear or light areas of photographic images. Sometimes, sulfurous gases from the air, such as in smoky rooms or

in areas heated by gas or coal, may hasten the sulfiding of the silver of the image. Early sulfiding may be detected as a metallic sheen on the surface of the silver image. Continued sulfiding of the silver image causes a progressive change from the dense black image of negatives to purplish-black to brownish-black to brown and yellowish-brown. Faded print images are usually yellowish-brown or yellow. A yellowish-brown or yellow stain may discolor the clear areas of negative and print images. There may be an apparent loss in density when enough of the silver image has been converted to silver sulfide. (See Figure 1.)

Fading due to sulfiding occurs more readily with fine-grained than with coarse-grained images. Because of their fineness of grain and the difficulty of thoroughly washing paper prints, silver images on photographic paper are usually more susceptible to attack than film images. In general, chloride

Figure 1. The silver image is remarkably stable if properly processed and then stored under suitable conditions. This photograph (dated 1883) from the author's collection shows one kind of image attack found in early photographs: small, brown sulfide spots that here are most evident in the dark sky or dark clothing.

paper emulsions produce images more susceptible to fading than those from silver bromide emulsions. Sometimes emulsion makers attempt to increase the resistance of emulsion preparations by using silver iodide washes near the end of the emulsion preparations for chloride, chlorobromide, and bromide emulsions, especially if the products are to be unwashed or are for archival purposes. Emulsion addenda, often containing organic sulfur compounds, are often added to protect the processed silver image from the attack of the decomposition products of the unstable thiosulfates. Attack by peroxides on the silver image may be inhibited, according to British Patent 1,156,167, by the incorporation of nondiffusing disubstituted hydroquinones (such as 2-octadecyl-5-sulfohydroquinone potassium salt) in the emulsion layer.

EFFECT OF COMPOSITION OF FIXERS UPON REMOVAL OF THIOSULFATE AND SILVER THIOSULFATES BY WASHING

The removal of thiosulfate and silver thiosulfates from the emulsion layer might seem to be solely the function of the conditions of washing. Photographic investigators began to note early, however, that the nature of the processing solutions appeared to be a factor in the rate of removal of the thiosulfate and silver thiosulfate during the washing. Johannes Gaedicke[1] has been credited with the observation in 1900 that alum-hardened plates required more washing than nonhardened plates. In 1912, and later in 1917, Lüppo-Cramer[2,3] pointed out that a nonhardening acid fixing bath washed out more slowly than a plain thiosulfate solution, such as was used by A. Vincent Elsden[4] in his studies. In 1926 K. C. D. Hickman and D. A. Spencer[5] found that hardening with formaldehyde did not alter the time of washing but hardening with potassium alum caused retention of the thiosulfates in the gelatin layer.

These early observations, often inconsistent, led J. I. Crabtree, G. T. Eaton, and L. E. Muehler[6] to study the effect of the composition of present-day processing solutions upon the removal of thiosulfate and silver thiosulfates by washing. This extensive investigation indicated that the composition of developers, ranging from Kodak D-76, DK-60a, D-72 (1:1) to the D-7 pyro formulation, did not influence the rate of removal of thiosulfate or silver thiosulfate from film fixed in Kodak F-5 fixing bath. The composition of stop baths (water, 2% acetic acid or 3% chrome alum, Kodak SB-3) neither retarded nor hastened the washing of film fixed in the F-5 fixing bath.

The composition, pH, and state of exhaustion of the fixing bath were found to be primary factors influencing the rate of washing.

Kind and Concentration of the Fixing Agent

The concentration level of sodium thiosulfate in the fixing bath did not vary the rate of removal of the thiosulfate from the emulsion layer. Substitution of equimolecular (14.4%) and semimolecular (7.2%) concentrations of ammonium thiosulfate was made for the sodium thiosulfate in the Kodak F-5, F-23, and F-24 fixing baths with an adjustment to maintain the normal pH of these solutions. The substitution in the F-5 formulation showed that the rate of removal of thiosulfate by washing was equal for the 7.2% ammonium thiosulfate and the normal sodium thiosulfate in the F-5 bath, but, after fixing in the 14.4% ammonium thiosulfate bath, the washing rate was 30% greater. No significant washing differences were noted between sodium and ammonium thiosulfate in the chrome alum (F-23) or the nonhardening (F-24) fixing baths. Any differences in the retention of silver thiosulfates were not large enough to be detected.

Effect of pH of the Fixing Bath

A protein such as gelatin possesses both acidic ($-COO^-$) and basic ($-NH_3^+$) groups. The acid groups can form protein salts; the basic groups can form proteinates. Gelatin exists as a charged molecule, either positive or negative, except at a condition called the isoelectric point, where the molecule is neutral. At this point, all of the basic groups are positively charged and an equal number, but not all, of the acidic carboxylic groups are negatively charged. The isoelectric point for lime-treated gelatins used in photographic emulsions may vary from pH 4.7 to 5.2. An isoelectric point of 4.8 or 4.9 has been reported for the commonly used lime gelatins in photographic emulsions.

Below the isoelectric point all of the basic groups will continue to be positively charged, but some of the acidic carboxylate ions ($-COO^-$) are converted to neutral carboxyl ($-COOH$) groups. Thus, the gelatin becomes increasingly more positive as the acidity is increased below the isoelectric point. Above the isoelectric point more carboxyl groups ($-COOH$) are converted to carboxylate groups ($-COO^-$), but the positively charged basic groups ($-NH_3^+$) are converted to uncharged amino groups ($-NH_2$). As the pH is raised above the isoelectric point, the gelatin molecule becomes increasingly negatively charged.

Below the isoelectric point (pH = 4.9) the gelatin is positively charged, and this charge attracts and holds negative ions such as thiosulfate or silver thiosulfates. Above pH 4.9 the gelatin is negatively charged. The thiosulfate ions are no longer retained, but positive ions, such as sodium or potassium, are then held by the gelatin. The acidity or the pH of fixing bath compositions

Table 1. Effect of Fixing-Bath Acidity upon Thiosulfate Removal[7]

Type of Bath	pH	Thiosulfate Content (mg/in.^{2})	
		10-min Wash	25-min Wash
Potassium alum–boric acid (Kodak F-5)	4.1	0.2	0.08
Potassium alum–boric acid (Kodak F-10)	4.6	0.12	0.06
Potassium alum–boric acid (Kodak F-6)	4.9	0.02	Nil
Chrome alum (Kodak F-23)	3.1	0.02	Nil
Nonhardening (Kodak F-24)	5.6	Nil	Nil

is fixed by the chemical balance to secure optimum fixation rate, hardening, and exhaustion life, as well as avoiding conditions that promote sulfurization or sludging. A number of practical fixing baths were studied by Crabtree, Eaton, and Muehler,[7] who related hardening and solution pH to washing effectiveness. (See Table 1.)

The removal of thiosulfate by washing increased as the pH of the fixing bath increased to pH 4.9. At pH values above 4.9 the thiosulfate was not retained. The chrome alum fixing bath has the lowest pH (3.1), but the retention of thiosulfate by films fixed in this bath was comparable to the results given by the nonhardening F-24 fixing bath of pH 5.6. This indicated that the effect of pH of the fixing bath is of primary importance when the bath contains potassium alum as the hardening agent. With photographic prints the rate of washing differed only during the very first minutes, after which the rate was the same regardless of the composition of the fixing bath. The washing of photographic prints involves other factors that influence the removal of thiosulfates from the photographic material. (See Figure 2.)

Effect of Hardeners in Fixing Baths

It was concluded[7] that "The hardeners are believed to tan the gelatin through the formation of some complex of unknown composition. The pertinent data indicate that the complex behaves exactly similar to gelatin with respect to isoelectric point and the retention of hypo. The data indicate that the potassium alum–gelatin complex is capable of adsorbing relatively large

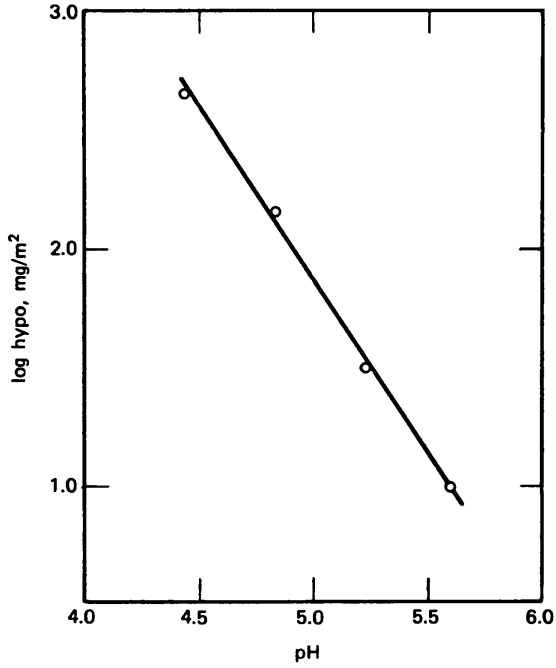

Figure 2. The effect of pH of the alum-hardening fixing bath on the thiosulfate (hypo) residue of Kodak Verichrome Pan film after a single, 4-min wash in deionized water. Note that the hypo residue is plotted on a log scale (1.0 equals 10 mg thiosulfate per square meter, 2.0 equals 100 mg/m²). [G. I. P. Levenson, *J. Phot. Sci.*, 15: 217 (1967).]

quantities of thiosulfate, whereas the chrome alum-gelatin complex apparently does not adsorb thiosulfate."

The hardening of gelatin by potassium alum may involve the precipitation of alumina or a compound with gelatin, an alumina complex. This complex binds or mordants thiosulfate ions much more strongly than does the negatively charged gelatin alone. S. E. Sheppard, Felix A. Elliott, and S. S. Sweet[8] concluded that "hardening is effected by Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ ions interacting with negative gelatin ions (including such complexes as $3Al(OH)_2^+ \cdot Al(OH)_3$). This necessitates the existence of gelatin anions at pH 4.8, but this is possible in the neighborhood of the isoelectric point." The formation of "aluminum gelatinates" requires the attraction of positively charged aluminum ions to gelatin that still has some negative charges (as near the isoelectric point as possible). At less acid conditions just above the isoelectric point, other forms of aluminum ions may exist, such as the negatively charged AlO_2^- ions. Hardening by potassium alum is thus limited to a

very narrow pH range near the isoelectric point of the common gelatins used for emulsion preparation. In this pH range conditions are suitable for the required ionic forms.

According to T. H. James and George C. Higgins,[9]

> It is probable that some type of aluminum-gelatin complex formation occurs in which the aluminum ion (or possibly an intermediate hydrolysis product) reacts with the $-COO^-$ groups of the gelatin chains to form crosslinkages between the polypeptide chains. This reaction increases the forces holding the chains together in the three-dimensional network of the rigid jelly. According to this view, three factors operate to produce a maximum in the hardening curves: (1) the free —COOH groups of the gelatin end and side chains become increasingly ionized to $-COO^-$ with increasing pH; (2) the concentration of aluminum ions decreases with increasing pH because of the formation of insoluble hydrous alumina, $Al_2O_3 \cdot x(H_2O)$, and related basic aluminum sulfites and sulfates; (3) the formation of colloidal alumina particles at the surface of the gelatin inhibits the penetration of aluminum ions into the gelatin because the colloid adsorbs the ions. The last two effects diminish the rate of hardening and, as they increase in magnitude, they eventually outweigh the first effect, and thereby account for the existence of the maximum in the hardening curve."

This concept of aluminum hardening is also stated by D. H. O. John and G. T. J. Field.[10]

Once formed, the aluminum-gelatin complex binds thiosulfates tenaciously, presumably through the unsatisfied positive valence attraction of some of the aluminum ions held by the gelatin. The chrome alum–gelatin complex does not retain the thiosulfate as strongly upon washing. Chromium ions form crosslinkages with both the $-COO^-$ and NH_2 groups of gelatin and apparently the chromium-gelatin complex does not possess sufficient residual electrostatic attraction to hold the thiosulfates during washing.

Effect of Exhaustion of the Fixing Bath

One important change in the composition of a fixing bath during use is the increase of the silver thiosulfate in the solution. For paper prints the safe limit for the silver content of an exhausted fixing bath is about 1.5 g/liter; for exhausted film fixing baths the silver content may be about 7 g/liter, although in practice this value may be exceeded sometimes.[11] Another change may occur: the pH of the solution may rise because the alkaline developer may be carried into the acid fixing bath. If an adequate water rinse or acid stop bath is used after development, the pH rise of the fixing bath is slight. Transferring the photographic material directly from the developer to the fixing bath causes a rapid increase in pH of the solution. In addition, hardening action is greatly decreased and sludging may occur if the solution pH increases above 6 for potassium alum baths or above 4 for chrome alum baths.

It was concluded by Crabtree, Eaton, and Muehler[7] that "These two changes, occurring with exhaustion, have a very definite effect upon the removal of residual silver and hypo from the film by washing. If the pH of a fixing bath is maintained during exhaustion at its original pH value and this value is below pH 4.9, both silver and hypo are removed very slowly as compared with the removal after the use of baths at pH values above 4.9. When the fixing bath is better than two-thirds exhausted and the pH is below 4.9, a small quantity of silver and hypo is never removed by washing, but as soon as the pH exceeds 4.9 these last traces of silver and hypo can be readily washed away."

Even with exhausted chrome alum fixing baths there is a small amount, though less than with potassium alum baths, of silver and hypo which is not removed by washing as long as the fixing-bath pH remains below 4.9. The washing of photographic materials fixed in well-used hardening fixing baths cannot remove the silver thiosulfate and thiosulfate ions that have been adorbed by the gelatin and the gelatin-hardener complex. It has been suggested that the adsorbed silver may be "in the form of a negatively charged complex silver thiosulfate ion which appeared to contain one thiosulfate radical and one atom of silver."[7] (See Figure 3.)

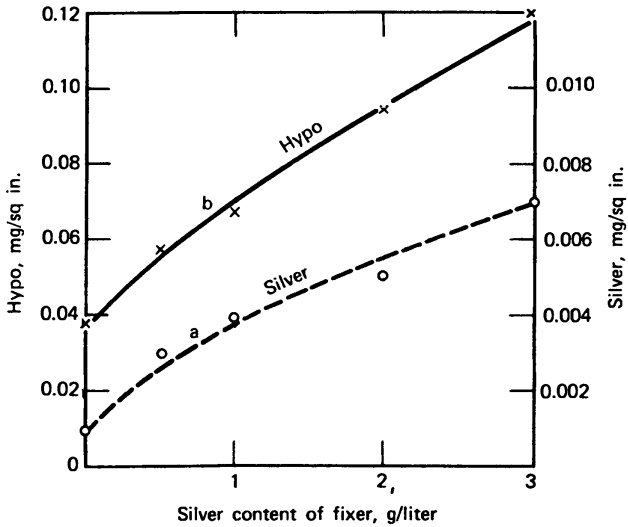

Figure 3. Silver (*a*) and thiosulfate (hypo) (*b*) content of a photographic print is given as a function of the silver content of the fixing bath. A stop bath was used to maintain the acidity of the fixing bath. Kodak Velox paper, F-3, single weight, was fixed for 10 min in Kodak F-5, then washed for 30 min in 40°F water. Both silver and thiosulfate content retained in print increase with silver content of fixer. [J. I. Crabtree, R. W. Henn, and R. F. Edgerton, *Phot. Sci. and Tech., PSA J.*, 19B: 14 (1953).]

The degree of hardening of the gelatin increases with time to a maximum when the film emulsion layer is immersed in a potassium alum fixing bath (pH below 4.9). As the degree of hardening increases, the concentration of the alumina in the gelatin increases, resulting in more and more of the thiosulfate and silver thiosulfate ions being bound to the gelatin-hardener complex. Most films are sufficiently hardened in about four times the time to clear; extending fixing times further in a potassium alum bath below pH 4.9 has little advantage. Fixing longer than this may still increase the hardening of some film emulsions but with a resultant increase in the amount of silver thiosulfate that cannot be removed by washing, especially if the fixing bath is nearing exhaustion.

TWO-BATH FIXATION AS AN AID TO WASHING

Film emulsions begin to retain silver thiosulfates when a potassium alum fixing bath (pH below 4.9) is about half exhausted; paper prints begin to retain silver thiosulfates with the first print processed.

The adsorption of thiosulfate and silver thiosulfate ions may be reversed by raising the pH of a single fixing bath or one of a combination of fixing baths above the isoelectric point of gelatin. In practice, this may not be possible. Silver thiosulfate complexes may also be removed from emulsion layers by immersion in a fresh fixing bath that contains a very low concentration of silver thiosulfate ions or none at all.

Early in the history of photography many investigators of silver image stability proposed the use of two fixing baths in succession. The second bath must be relatively unused so that it can effectively wash out the adsorbed silver thiosulfates that were retained during treatment in the more exhausted first bath. By 1882 W. Jerome Harrison,[12] in his book, *The Chemistry of Photography*, was listing as a maxim for fixing, "Use *two* fixing baths" (italics in the original). A suggestion for the complete fixation of photographic prints by the Lumières and Seyewetz[13] involved a 5-min immersion in each of two fixing baths, each fixing period followed by at least a 1-hr wash in water. F. B. Grundy and A. Haddon[14] proposed a 5-min water wash between the two fixing baths.

At the beginning of the fixation with two fixing baths in succession, the silver accumulates very rapidly in the first bath but only starts to increase rapidly in the second bath after one hundred 8 × 10-in. films per gallon have been processed. With film processing, the second bath may be selected to improve the efficiency of washing, such as (1) a nonhardening fixing bath below pH 4.9, (2) a hardening or nonhardening fixing bath buffered above pH 4.9, and (3) a chrome-alum fixing bath. There is a carryover of solution

from the first to the second bath, resulting in its chemical contamination if the two baths are different. The use of two hardening baths of identical composition does allow the second bath to be substituted easily for the first bath as the first bath becomes exhausted. A number of cycles of *discard first bath—substitute second bath for first—replace second bath with fresh fixing solution* may be carried out, providing economy of chemical cost as well as promoting efficient removal of adsorbed thiosulfates.

The maximum practical degree of exhaustion of a film or print fixing bath used as the first bath in the two-bath system is reached when the bath requires about twice the time to clear of a fresh fixing bath. For film, this corresponds to a bath containing about 6 g silver per liter; for paper prints, the fixing bath should not contain more than 1.5 to 2.0 g silver per liter of solution.[7] These maximum levels of silver content of the fixing bath are modified for different requirements for the necessary stability of the silver photographic image.

The keeping life of the photographic image is usually classified for two levels of use: (1) commercial, with a life of a limited number of years, and (2) archival, for maximum image permanence during long-time storage. Suggested maximum permissible levels of silver in the fixing bath or the photographic material for both commercial and archival use are listed in Table 2 as given by Crabtree, Eaton, and Muehler.[6] Suggested maximum permissible levels of residual hypo are given in Table 3.[6] For archival image stability of images on cellulose ester base, American National Standard PH 1.28-1969[15] specifies the maximum permissible concentration of thiosulfate (as anhydrous sodium thiosulfate) to be 1 μg/sq cm for fine-grain film and 3 μg/sq cm for medium-grain camera films and coarse-grain X-ray films. The maximum image permanence occurs, however, when all thiosulfate and silver thiosulfates have been removed.

The elimination of thiosulfate and silver thiosulfates from the gelatin emulsion layer of films and papers occurs in about the same manner. The complete removal of these ions is much more difficult for paper prints than for photographic films, however. Photographic papers consist of paper fibers to form the base with a gelatin layer or a layer of barium sulfate and other constituents to form the intermediate layer. The emulsion layer is applied on top of the gelatin or baryta layer. All three—the paper base, the intermediate gelatin or baryta layer, and the emulsion layer—retain thiosulfate and silver thiosulfates. The paper base and the baryta layer retain greater quantities than the gelatin emulsion layer. Fixing baths with pH values above or below the isoelectric point of gelatin have little or no effect upon the retention of thiosulfate or silver thiosulfates by photographic prints when the retained thiosulfates are in the paper base or baryta layer. Resin-coated paper bases, though more expensive, have very little thiosulfate retention, thus shortening the washing period considerably.

Table 2. Suggested Maximum Permissible Concentrations of Silver; pH of Fixing Bath Maintained Below 4.9

	Commercial Use	Archival Use
	Single Bath	
Films:		
Fixing bath	1.5 g/liter (twenty-five 8 × 10-in. films/gal)	0.2 g/liter (two 8 × 10-in. films/gal)
Film	0.01 mg/sq in.	Nil
Paper:		
Fixing bath	0.3 g/liter (thirty 8 × 10-in. prints/gal)	0.05 g/liter (five 8 × 10-in. prints/gal)
Paper	0.005 mg/sq in.	Nil
	Two Fixing Baths	
Films:		
Fixing Bath No. 1	6.0 g/liter (sixty to seventy 8 × 10-in. films/gal)	3.5 g/liter (forty 8 × 10-in. films/gal)
Fixing bath No. 2	0.5 to 1.5 g/liter	0.2 g/liter
Film	0.01 mg/sq in.	Nil
Paper:		
Fixing bath No. 1	2.0 g/liter (two hundred 8 × 10-in. prints/gal)	0.80 g/liter (seventy 8 × 10-in. prints/gal)
Fixing bath No. 2	0.3 g/liter	0.05 g/liter
Paper	0.005 mg/sq in.	Nil

Table 3. Suggested Maximum Permissible Concentration of Hypo[6]

	Commercial Use (mg/sq in.)	Archival Use (mg/sq in.)
Films:		
Eastman motion picture films:		
Fine-Grain Duplicating Positive Film, Type 1365	0.02	0.005
Fine-Grain Release Positive Film, Type 1302	0.05	0.01
Super-XX Panchromatic Negative Film, Type 1232	0.20	0.05
Photofinishers and amateurs	0.15 to 0.25[a]	0.05
Eastman X-ray films:		
No screen	0.40 to 0.50[a]	0.10
Blue Brand	0.25 to 0.40[a]	0.05
Industrial, type A	0.15 to 0.25[a]	0.05
Prints:		
Double weight	0.20 to 0.25	Nil
Single weight	0.10 to 0.15	Nil

[a] The coatings on many of these films consist of either (1) emulsion on one side and gelatin on the opposite side, or (2) emulsion on both sides (X-ray). The values above represent the hypo content of the coating on only one side of the film, so that when employing the mercuric chloride test which determines the total hypo, these values should be doubled.

More thiosulfates are retained per unit area by a photographic paper with a fibrous base than a photographic film. The finely divided silver of print images, especially those on warm-toned photographic papers, is especially susceptible to degradation by the thiosulfates that are mostly retained in the baryta or paper base. Degradation of the silver of print images is quickly apparent, as the print image is on a white paper base that makes the discoloration evident.

With regular photographic paper having a baryta layer, Crabtree, Eaton, and Muehler[6] used nonhardening (F-24) and hardening (F-5) fixing baths to show that "(1) pH values in the range of 4.0 to 5.6 had little effect on the rate of removal of hypo and silver, (2) the rate of removal was greater after fixing in F-24 as compared with F-5, only during the early stage of washing, and (3) small amounts of residual hypo and silver in the base and baryta coating were

not removed by very prolonged washing." These investigators concluded, "The most practical and efficient method of removing the last traces of both silver and hypo from prints is to employ two or three successive baths. A second bath is imperative in any fixing operation and a fresh third bath is imperative in the preparation of permanent prints when the residual silver content must be zero."

The two-bath system of fixation should be limited to five cycles because contamination, dilution, evaporation, sludges and slimes, and other deleterious factors should not be allowed to endanger the highest possible print permanence. In the last four cycles, the second bath becomes the first bath for the processing of the next two hundred 8 × 10 prints per gallon of solution. Because the second bath has already been used for the previous two hundred 8 × 10 prints, the possibility exists that the silver content of the system may rise to higher levels during the remaining cycles of fixation. Carryover from the first bath, previously used as the second bath, could possibly result in higher silver concentrations accumulating in the fresh second baths during the third, fourth, and fifth fixation cycles. This possibility was investigated by J. I. Crabtree, R. W. Henn, and R. F. Edgerton.[16] After two hundred 8 × 10-in. prints had been processed during the first cycle with two 1-gal fixing baths, the silver content of the first fixing bath was 2.2 g silver per liter and 0.9 g/liter in the second bath. The second cycle starts with a bath having 0.9 g silver per liter, so that solution carryover into the second fresh bath will be at a higher silver level than at the start of the first fixation cycle. After 200 more prints were fixed, the silver content of the second bath was 1.1 g/liter, slightly more than at the end of the first cycle. During the remaining three cycles the silver content of the second bath did not increase appreciably, indicating that near-equilibrium conditions existed.

SINGLE-BATH FIXATION AND WASHING

When a single fixing bath is employed, only fifty 8 × 10 prints can be processed in a gallon of bath for comparable retained silver to two hundred 8 × 10 prints in the two-bath system. If the minimum staining tendency for prints is required, only thirty 8 × 10 prints should be processed per gallon when a single fixing bath is used, as the silver level after thirty prints is the same as the silver content of the second bath after 200 prints, although one hundred 8 × 10 prints are now allowed for commercial processing quality.

In the single-bath system it would take 2 gal of fixing bath to treat 200 prints (100 prints per gallon yielding commercial quality of silver retention). This is equal to 200 prints from the two1-gal baths of the two-bath system, but the silver content of the second bath will be only one-third that of the

single bath, providing prints of greater stability because of lowered retained silver content. The second bath of the two-bath system is then reused, cutting chemical cost from one-third to one-half, and the silver content will be no more than one-half that of the single bath. These savings led Crabtree, Henn, and Edgerton to remark, "The two-bath recycling system can therefore mean 'twice the quality at half the cost'."

PRACTICAL RECOMMENDATIONS FOR FIXATION

Single-Bath Fixation

Film

1. Film to be fixed should be in reels or hangers so that the solution has free access to the surface. If sheets of film are to be fixed in a tray of solution, the sheets must be separated constantly during the fixing period.
2. Film should be agitated at intervals during the fixing period.
3. Do not exceed recommended fixing time, especially if the fixing bath is fresh. Fixing is very rapid in fresh solutions. Recommended times include a safety factor that insures that even a nearly exhausted bath will be satisfactory in its used condition.
4. About one hundred 8 × 10 films, or equivalent, can be fixed in a gallon of fixing bath. Film should not be treated in a fixing solution containing more than 6 g silver per liter of solution. This point in exhaustion is reached approximately when the film requires twice the time to clear as in a fresh bath.

Paper Prints

1. If paper prints are fixed in a tray, use a tray large enough to permit easy handling of the prints—for example, no more than twelve 8 × 10-in. prints in a 16 × 20-in. tray.
2. Separate and agitate prints during the fixing period, making sure that the prints are below the surface of the liquid. It is important that the fixing solution is able to reach the center of each print.
3. Print fixing time in sodium thiosulfate baths* is about 5 to 10 min. Do not exceed the 10-min maximum, as the silver image of many photographic papers is especially susceptible to attack by the thiosulfate. Prolonged soaking in a fixing bath results in the adsorption of silver thiosulfates by

* Ammonium thiosulfate rapid fixers can be used if sufficiently diluted—for example, 1:3 for films but 1:7 for prints.

the paper fibers. This retained silver is difficult if not impossible to remove by washing.

4. Discard the single fixing bath after thirty 8 × 10-in. prints have been processed in a gallon of solution, if prints with a minimum tendency to stain with age are required. Print fixing baths should be discarded when the solution contains 2 g or more of silver per liter of solution.

Two-Bath Fixation

Paper Prints

1. After development, immerse prints in an acid stop bath, pH 3.5 to 5.5, such as 2% acetic acid, Kodak SB-1a, or SB-5a, for at least 30 but not more than 60 sec. On paper processing machines, Kodak F-24 fixing bath may be used in place of the acid stop bath.[17]
2. Drain prints, individually or as a clump, for 5 sec or longer.
3. Immerse prints, individually if possible, in the first of two fresh fixing baths for 3 to 5 min.
4. Keep prints separated and agitate at intervals during the fixing period.
5. Drain prints for at least 5 sec (IMPORTANT), preferably longer, before immersing in the second fresh fixing bath.
6. Keep prints separated and agitate at intervals during the 3- to 5-min period in the second fixing bath.
7. Drain prints for 5 sec, preferably more.
8. Wash single-weight prints for 30 min, double-weight prints for 60 min, in running water at 65 to 70°F, with the water changing once every 5 min.
9. If two 1-gal fixing baths are used, the first bath is discarded after the processing of two hundred 8 × 10-in. prints.
10. The second fixing bath is then moved to replace the discarded first bath, and a fresh gallon of fixing solution is used for the second bath.
11. Both solutions should be discarded after 5 cycles—that is, after one thousand 8 × 10-in. prints have been processed. If one thousand prints are not processed during one week, discard both solutions and start the next week with fresh fixing baths.
12. The condition of the second fixing bath may also be determined by chemical means using commercially available hypo testing outfits or by spot-testing methods.

SULFIDING OF THE IMAGE DURING FIXATION

The photographic image is fixed by converting the unused silver halides to soluble silver thiosulfates. Even if all the silver thiosulfates, the remaining thiosulfate, and other water-soluble salts could be removed by washing in

water, the remaining image might not be pure silver. This fact became evident when a processed film image, after fixation in a thiosulfate fixing bath, was bleached in chromic acid solution; that is, the metallic silver of the image was converted to the ionic form and then removed from the emulsion layer. A brown residual image remained and, according to Lüppo-Cramer[18] in 1908, consisted of silver sulfide. The sulfide image was not formed if the photographic material was fixed in strong potassium bromide or in potassium cyanide solutions.[19]

Lüppo-Cramer concluded, as have others,[20] that thiosulfate from a thiosulfate fixing bath was adsorbed to the metallic silver of the image, in proportion to the quantity of silver, and this retained thiosulfate was converted to silver sulfide during the bleaching of the metal to the ionic form. The composition of the residual image after bleaching was shown by A. and L. Lumière and A. Seyewetz[21] to depend upon the composition of the photographic emulsion. The residual image from pure chloride, pure bromide, or chlorobromide emulsions was composed almost entirely of silver sulfide; the residual image from bromoiodide emulsions consisted of substantial amounts of silver iodide but only a little silver sulfide.

In photographic images produced from emulsions without iodide, the thiosulfate is so strongly adsorbed to the silver of the image that the thiosulfate cannot be removed by prolonged washing or by oxidation with alkaline peroxide hypo eliminator, such as HE-1.[22] The thiosulfate was converted to silver sulfide in the bleaching bath because of the availability of a large concentration of silver ions. At most, 5% of the original film negative was estimated to be converted to silver sulfide.

The percentage of the original silver sulfided during fixation is considerably higher for photographic papers. Chester I. Pope[39] reported, "In the region of high-silver densities or full exposure the amount of sulfiding of the silver image is about 25 percent for the photocopy paper, about 17 percent for the contact paper, and about 28 percent for the enlarging paper. At lower silver densities the amount of sulfiding of the silver image is about 20 percent for a density of 0.6 for the photocopy paper, about 9 percent for a silver density of 1.0 for the contact paper, and about 14 percent for a silver density of 1.0 for the enlarging paper. The percentage of the silver sulfided increases as the silver density in the image increases up to the high densities."

The amount of sulfiding of the silver image in the high-density areas was either 5 or 7% for two microfilms. This image sulfiding during fixation has a negligible effect on the permanency of the images on microfilm. The high percentage of sulfiding of images on paper, however, means that further sulfiding of the image by retained thiosulfates in the gelatin or paper base must be avoided or image coloration will become apparent in the low-density (highlight) areas of the prints.

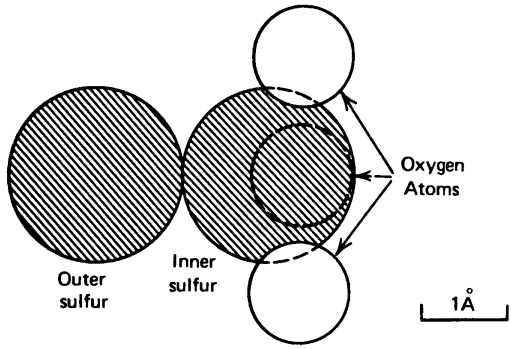

Figure 4. A representation of the thiosulfate ion, $S_2O_3^{2-}$, showing the easily removable outer sulfur atom. [P. A. Block and G. W. W. Stevens, *J. Phot. Sci.*, 9: 331 (1961).]

The inhibition of image sulfiding with bromoiodide emulsions is thought to be due to the preferential adsorption of iodide ions to the surface of the silver image. This would limit the amount of thiosulfate that could be adsorbed, because the suitable sites would be occupied by the iodide. During bleaching of the silver image the iodide would form silver iodide, but this compound would be solubilized and no residual image would remain.

The thiosulfate ion, $S_2O_3^{2-}$, consists of two sulfur atoms attached to each other with three oxygen atoms clustered about one sulfur atom (called the inner sulfur atom). (See Figure 4.) Thiosulfate ions were prepared with either the inner or the outer sulfur atom radioactive.[23,24] By studying the amount of radioactivity produced by the labeled thiosulfate atoms that were adsorbed to image silver, it was shown that most adsorbed thiosulfate had already suffered rupture of the sulfur-to-sulfur bond before the bleaching of the image. The release of the labile outer sulfur atom was essentially complete in less than 15 min at room temperature. The inner sulfur atom with its oxygen atoms is readily removable by washing in water. The silver sulfide formed by the attack of the outer sulfur upon the silver of the image was resistant to removal even by the action of potassium cyanide. It is thought that the orientation of the silver sulfide on the surface of the silver image may be such as to make the silver of the silver sulfide unavailable for reaction with the cyanide.

Once formed, this silver sulfide cannot be removed by washing or by baths containing oxidizing agents. The formation of the silver sulfide may be inhibited, however, by the addition of potassium iodide to the fixing bath. In 1930, Alexander Murray[25] said that Ross and Crabtree had suggested the use of $\frac{3}{4}$ oz. of potassium iodide per gallon of fixing solution. From 0.1 to 1.0% potassium iodide in the fixing bath has been proposed for use with

positive film.[26] One gram of potassium iodide was added by Chester I. Pope[39] to each liter of an acid fixing bath, preventing most of the normal sulfiding of the image silver that would be present after bleaching the image. Pope reported, "The density of the silver sulfide ranged from 0.02 to 0.04 for contact and enlarging papers which normally yielded a silver sulfide density of 0.2 to 0.25. The density of the silver sulfide was about 0.005 for two microfilms which normally yielded a silver sulfide density of 0.10 to 0.15." The presence of even the small quantities of potassium iodide in the fixing bath increases the fixing time and shortens the useful life of the bath.

HYPO ELIMINATION

Thiosulfate elimination can be accelerated by the use of two classes of chemicals: (1) compounds that act by physically displacing the thiosulfates from the photographic material by an ion-exchange action, and (2) compounds that react with the thiosulfate, usually oxidizing it to a form that is more soluble or more diffusible during the subsequent washing in water.[27] The first class of compounds, which do not react chemically with the thiosulfate, are usually called hypo clearing compounds or washing aids. The second class of compounds, the oxidizers, are called hypo eliminators.* Both types of compounds have as their objective the improvement of silver image permanence by the reduction of the quantity of silver thiosulfates and thiosulfate that is retained by the photographic material.

Pure water is a relatively poor washing medium for developed-and-fixed photographic materials.[28] Where the local water supply is of a peaty nature (low dissolved-salts content), difficulties may be experienced in washing photographic products that do not occur in areas where the tap water is of moderate hardness (higher salts content). Salts normally found in natural waters were added to demineralized water and the effectiveness of such water was studied by G. I. P. Levenson[28] by measuring the thiosulfate residue after a 4-min washing of film. He concluded, "The most important component of tap waters favouring rapid washing would appear to be the alkali bicarbonate." Increasing the pH of the wash water with sodium hydroxide, sodium sulfite, or sodium bicarbonate up to a pH of about 9 improved the rate of washing. Swelling of the emulsion layer appeared to be of secondary importance. The solutes in the wash water were most effective when the film had an aluminum-hardened emulsion layer.

* The term "hypo eliminator" *usually* refers to chemical treatments that oxidize the thiosulfate.

Table 4. Effect of Various Solutions on Thiosulfate Residue in Positive Film[a] (4-Min Wash)[28]

Solution	pH at *M*/250	Effectiveness at *M*/250 Relative to Pure Water	Swell at End of Wash at *M*/250
Hydrochloric acid	2.45	0.6	12 μ
Sodium thiosulfate	5.6	0.95	—
Demineralized water	approx. 6	1.0	8
CO_2 saturated water	4.65	1.0	—
Sodium chloride	6.1	1.5	—
Sodium bisulfite (meta)	4.1	2.8	9.5
Sodium sulfate	6.4	14	10
Sodium bicarbonate	8.4	49	11.5
Sodium sulfite	9.2	87	10.5
Sodium hydroxide	11.6	89	17.5

[a] Dry emulsion thickness = 10 μ.

When a gelatin emulsion layer after fixation is washed with pure water, there are two stages of removal of the thiosulfates: (1) a first stage in which there is a rapid removal of most of the thiosulfates from the gelatin layer, and (2) a slow second stage during which the thiosulfates are removed by being replaced by ions contained in the wash water.[29] Pure water contains only H^+ and OH^- ions, and these ions exchange at a very slow rate with the adsorbed thiosulfate ions. In tap water of moderate hardness, bicarbonate and carbonate ions are more efficient in the removal of the thiosulfate by exchange displacement. (See Table 4.)

Salt Baths Aiding the Elimination of Thiosulfates

Sea Water

In 1903 Dr. O. Bayssellance[30] related how, while sailing on a steamer, he used sea water to wash his prints, using a final rinse in fresh water to remove the sea salts. Later, when he was no longer sailing, he made up a bath containing 30 g sea salt in a liter of water. Prints were immersed in this hypo

clearing bath for one-half to one hour, followed by three or four washes in fresh water. Dr. Bayssellance was not the first to recommend salt solutions for thiosulfate elimination. In 1889 Dr. Bannow[31] used immersion in a 10% solution of common salt, followed by two pure water baths, to "eliminate the hypo to perfection."

Sea water has been studied since that time as a means for the removal of the retained thiosulfates.[32,33] Sea water contains about 3.5% of various salts, over 25% of these being sodium chloride and more than 3% magnesium chloride. A number of carbonates, nitrates, sulfates, bromides, and other salts are also present in small quantities.

Sea water (from off the Maine coast) was found to be much more effective than tap water (Rochester, N.Y.) for the removal of thiosulfates from film or paper prints. G. T. Eaton and J. I. Crabtree[34] reported that "washing times of several hours in running fresh water reduced the residual hypo content of double weight prints to an average low value of 0.07 mg per square inch whereas sea water, in these tests, removed the hypo completely in 50 minutes." Kodak Verichrome pan film washed 10 min in sea water had a thiosulfate content of 0.005 mg/sq in., but 0.080 mg/sq in. remained after washing the film for 30 min in fresh water.

Sea water residues cannot be left in film or prints because the remaining chloride salts cause, in the presence of the thiosulfates, rapid fading of the silver image under storage conditions of high humidity and temperature. In addition, magnesium chloride retained from the sea water takes up water from the air (hygroscopic), causing the gelatin emulsion layer of films and prints to become sticky. If the prints are to be made glossy by pressing against a smooth surface, such as on a ferrotyping tin or on a gloss print dryer, the residual sea salts in the emulsion layer will be transferred to the ferrotyping surface, with possible corrosion as the result. For these reasons, washing solely in sea water is impractical.

It is a practical and economical procedure, however, to wash in sea water for one-half the normal washing time suggested for fresh water, then wash for 5 min in running fresh water or two changes of 2 min each in fresh water that is agitated. The final fresh water rinse removes the residual salts from the photographic material, avoiding the accelerated image fading or emulsion tackiness that occurs with washing only in sea water.

Sodium chloride in sea water apparently acts by reacting with the adsorbed silver thiosulfate, releasing the thiosulfate ion and forming silver chloride.

$$Ag(S_2O_3)_2^{3-} + Cl^- \longrightarrow AgCl + 2S_2O_3^{2-}$$

The small amount of silver chloride is then solubilized by the excess chloride ions present in the sea water. Bromide and iodide ions are even more effective

than the chloride ions in eliminating silver thiosulfate, the effectiveness increasing as the solubility of their silver salts decreases.

Hypo Clearing Compounds

An ion that is adsorbed can be replaced by an ion having a higher valence (higher charged condition), but the adsorbed ion cannot be displaced by an ion having a lower valence.[35] If both ions have the same valence, the ion that is less concentrated will be replaced by the ion that is more concentrated. According to André Charriou,[35] the singly charged ions of water could not replace an adsorbed, doubly charged ion of thiosulfate. Solutions of most salts, such as of sodium chloride, have some effect, but those salts with ions having valences greater than one are the most effective in removing the thiosulfates adsorbed to the gelatin or to a gelatin-aluminum complex. The displacement of the thiosulfates is primarily the result of the negatively charged ion of a salt, and the positively charged ions (ammonium, magnesium, potassium, or sodium) have little effect.

Salt solutions containing monovalent negative ions, such as acetate, bromide, chloride, or nitrate, have been found to be less effective than ions with higher valences, such as phosphate, sulfate, and sulfite. A solution of sodium sulfite has a particularly high efficiency in removing adsorbed thiosulfates. Even when the normal alkalinity of sulfite solutions is reduced, the sulfite ion still is unusually effective in displacing adsorbed thiosulfates. This action is thought to be related, in part, to the chemical similarity between sulfite and thiosulfate ions, resulting in an easier interchange between these two ions.[36]

Immersion of films or paper prints in a 2% solution of sodium sulfite, following a 1- to 2-min rinse in water after two-bath fixation, has been recommended by Eugene Ostroff[37] for securing image permanence. Films and single-weight prints are treated for a minimum of 2 min; double-weight prints should be immersed in the 2% sulfite bath for at least 3 min. Film negatives require a 5-min water wash; single-weight prints need 10 min, and double-weight prints 20 min. (See Figure 5.)

A number of commercial washing aids that are salt solutions have been introduced for both small-scale and machine processing. These products appear to be essentially 2% sulfite formulations that contain sufficient sodium bisulfite to lower the pH of the solution to minimize emulsion swelling. Lowering the alkalinity of a sodium sulfite solution decreases the rate of thiosulfate elimination. The pH adjustment—ranging from about 5.8 to 7.2—represents a compromise in the desired properties of the sulfite bath. A sequestering agent may also be added to prevent the precipitation of the sulfite by the calcium ions contained in the water supply.

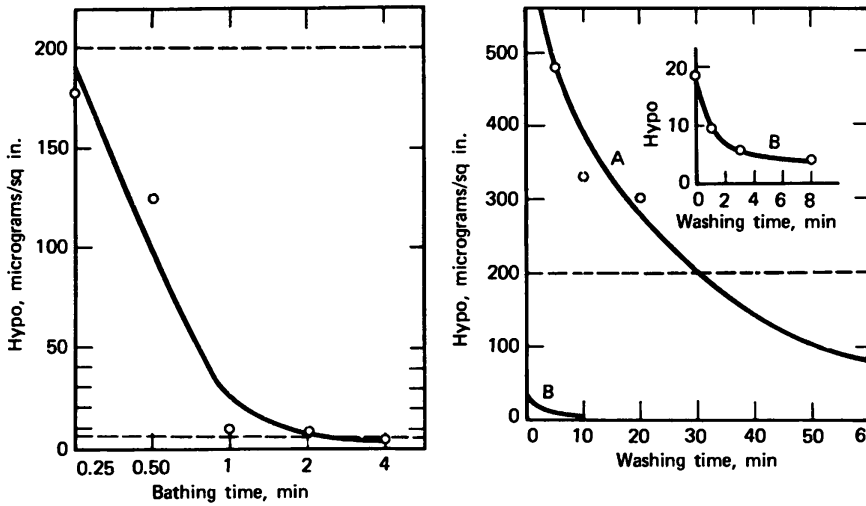

Figure 5. The effect of time of bathing in a 2% solution of sodium sulfite is shown (left) upon the retained thiosulfate (hypo) after washing. Sheet film was developed, fixed in F-5 fixing bath, bathed for the listed times, and washed for 5 min. The effect of varying the time of washing is indicated (right) after the film had been (A) washed immediately after fixation or (B) had been bathed for 2 min in 2% sodium sulfite before washing. Note that a 2-min immersion in the 2% sulfite solution, followed by only 1 min of washing, produced a residual thiosulfate content that was below that given by washing in water for more than 1 hr. [J. I. Crabtree and R. W. Henn, *J. SMPTE*, 65: 379 (1956).]

Silver image stability after the use of salt solutions as washing aids has been carefully evaluated. It was reported[36] that

A 1% solution of sodium sulfite or a 10% solution of sodium sulfate proved almost completely effective in eliminating hypo under these conditions of use, namely 2-min bathing, followed by 5-min washing.

Strips of fine-grain films and prints, which were treated in a sodium sulfate solution, washed and incubated have proved to have the same stability as films or prints washed to equal hypo content without a salt bath. When the salt employed was sodium sulfite, the treated images actually showed better stability than would be anticipated from their hypo content, presumably owing to some stabilizing action of the sulfite on the thiosulfate, just as sulfite is added to fixing baths to prevent the hypo from sulfurizing. Also, incubation tests have indicated that films bathed in a salt solution before washing have less tendency toward highlight staining.

Elimination of thiosulfates by the use of hypo-clearing salt baths has been widely adopted for machine processing of both black-and-white and color materials. Higher machine speeds, the use of less water for washing, and

some saving of space have resulted from the accelerated removal of the bound thiosulfates. A buffered sulfite clearing bath (pH = 5.8)

Sodium sulfite, desiccated	5.0 g
Sodium bisulfite	26.0 g
Calgon (Calgon Corp.)	1.0 g
Water to make	1.0 liter

containing a calcium-sequestering agent has been reported[38] to be useful in reducing the final wash time of the Eastman color print process. A final film pH of 5.7 and residual thiosulfate levels of less than 0.02 mg of anhydrous thiosulfate per square inch have insured normal dye stability.

Salt solutions remove thiosulfates by a mechanism that primarily involves ion displacement. The relatively few adsorbed thiosulfate ions are displaced by the very large number of ions present in the salt bath. Because of their close chemical similarity to thiosulfate ions, sulfite ions may form soluble double compounds with the thiosulfates. Sulfite may also combine with sulfur atoms that may have resulted from the dissociation of the thiosulfate, much as does the sulfite when it is present in an acid fixing bath.

The beneficial effect of salt solutions does not protect the silver image against attack by atmospheric gases of an unsuitable storage area. It has been suggested[48] that a selenium toner, such as 10 ml of Kodak rapid selenium toner, be added to each liter of the salt solution. The selenium toning will help protect the silver image against the attack of oxidizing gases in the atmosphere, but it may somewhat modify the tone of warm-toned papers.

Two salt baths have been formulated by Chester I. Pope[39] for the elimination of adsorbed thiosulfates.

Bath 1

Sodium sulfate, anhydrous	140 g
Ammonium hydroxide, 28% solution	2 ml
Water to make	1 liter

Bath 2

Sodium sulfate, anhydrous	71 g
Sodium sulfite, anhydrous	63 g
Water to make	1 liter

Film or paper, after fixation, is rinsed for 1 min in running water, then treated 10 min in either salt bath, and finally washed 30 min in running tap water.

Hypo clearing baths have been studied by Pope[40] for microfilm use where image permanence is necessary. Microfilm images were fixed in a fixing bath containing 8 g silver per liter (equivalent to a well-used fixing bath), washed 3 min in running water at 25°C, and then treated for 10 min at 25°C in one of the following solutions: (1) 6% sodium chloride, (2) 3% potassium bromide, or (3) 0.15% potassium iodide. The adsorbed thiosulfates were reported to be completely eliminated from all image densities by the solutions of potassium bromide and potassium iodide. Silver thiosulfate was still retained, however, in the high image densities after treatment with the sodium chloride solution.

The bromide or iodide ions react with the adsorbed silver thiosulfate, releasing water-soluble thiosulfate ions and forming silver bromide or silver iodide. These low-solubility silver halides may be solubilized if sufficient halide ions are present in the solution. A 3% potassium bromide or a $4\frac{1}{2}$% potassium iodide solution eliminated the thiosulfate completely, even in the high-density areas of the microfilm. In the $4\frac{1}{2}$% potassium iodide solution there was a sufficient concentration of potassium iodide to form the complex of silver iodide–potassium iodide, which was readily removed during washing.

A concentrated solution of 20% magnesium sulfate, 10% potassium bromide, and 0.3% sodium hypochlorite (NaOCl) has been patented (U.S. Patent 2,688,546) as a composition for thiosulfate elimination. This solution is diluted with five to 10 times its volume of water for use. For example, photographic prints without washing are transferred directly from the fixing bath, treated 5 min in the diluted composition, then washed 10 to 15 min "to remove all traces of the hypo." Another patented processing solution (U.S. Patent 3,598,588) uses a monochloro- or monobromo-substituted aldehyde or acid as a hypo-eliminating bath. After nonhardening fixation, photographic paper is washed for 1 min, then treated 2 min in a bath of 30 g sodium chloroacetate dissolved in a liter of water. The paper is then dried by glazing; no, or only negligible, thiosulfate is detectable.

The use of salt baths as washing aids introduces yet another solution into the processing cycle in an effort to overcome the thiosulfate-mordanting action of acid fixing baths with aluminum hardeners. Efforts appear under way to incorporate the thiosulfate-eliminating salts in the developer or fixing bath, thus avoiding the use of the separate salt bath. If a hardening agent, such as sodium glutaraldehyde bisulfite, is present at about 2% in the alkaline developer, sufficient hardening occurs during development so that some sites for hardening the gelatin are no longer available for acid alum hardening during the fixing period. The washing time is shortened because the mordanting of the thiosulfates by the alum-gelatin complex appears to have been limited by the prior aldehyde hardening. In alkaline monobaths the presence of sodium sulfite and other salts as well as aldehyde hardeners has resulted in the rapid washing of monobath-processed photographic materials.

Another approach to improve washing is to incorporate the hypo-clearing salts in the fixing bath. In a French patent Max Heilmann[41] proposed to add high concentrations, preferably 80 to 100 g/liter, of the salts of divalent or polyvalent acids to the fixing bath. Examples of suitable salts are sodium sulfite; sodium bicarbonate; disodium phosphate; sodium citrate; sodium, potassium, ammonium, or magnesium sulfate; and ammonium oxalate.

Adding 100 g sodium sulfate (anhydrous) to a fixing solution containing 175 g sodium thiosulfate pentahydrate and 15 g potassium metabisulfite per liter accelerated film washing about 60%. The addition of 100 g of sodium sulfate (anhydrous) to a bath containing 180 g of ammonium thiosulfate and 20 g of potassium metabisulfite per liter cut washing time to about one-half the time needed for the fixing bath without the sulfate. It is claimed that hardening by fixing baths containing aluminum hardeners is not inhibited. Presumably, the neutral salts compete with the hardener for adsorption sites on the gelatin, thus limiting the aluminum-gelatin complex that is formed. It is also possible that the salts contained in the fixing bath may be carried into the wash water to enhance its washing power.

U.S. Patent 3,008,828 proposed to use increased sulfite and bisulfite concentrations in acid-hardening thiosulfate fixing baths to improve the washout of the thiosulfate from the photographic material. One such fixing bath had the following composition:

Sodium thiosulfate (anhydrous)	50.0 g
Potassium alum	5.0 g
Sodium sulfite	5.0 g
Sodium bisulfite	100.0 g
Acetic acid (28%)	16.0 ml
Water to make	1.0 liter

Alkaline Baths

By 1854 the lack of permanence of paper prints had become so serious that the Photographic Society of London appointed a committee to study the "Fading of Positive Photographic Pictures upon Paper." This committee concluded, "It appears that the most ordinary cause of fading may be traced to the presence of sulfur, the source of which may be intrinsic from the hyposulfite left in the print, or extrinsic from the atmosphere, and in either case the action is much more rapid in the presence of moisture."[42] The committee's first report in 1855 failed to recommend any method to eliminate completely the retained thiosulfate.

One of the members of this committee, T. A. Malone,[43] proposed treating fixed prints with a strong solution of potassium hydroxide heated to about 180°F, then washing out or neutralizing the alkali. Another committee member, T. Frederick Hardwich,[44] suggested the avoidance of acid in the print. These were the first of many proposals to use alkaline baths to help free fixed photographic materials from image-degrading thiosulfates. Ammonia or the combination of ammonia with other chemical baths was proposed on several occasions.

In 1923 André Charriou[45] concluded that the ions of water could not displace the adsorbed thiosulfate from paper prints, even after 24 hr washing in water. Treatment of the prints in baths containing 5% sodium or ammonium bicarbonate caused a more rapid and more complete elimination of thiosulfate than was possible by washing.

E. Weyde[46] in 1935 proposed a maximum of 1 min immersion in a 1% (but not more than 1%) solution of sodium carbonate between the fixation and washing of photographic prints. She reported, "After 10 minutes' washing in running water, hypo is as completely removed from prints treated with the soda bath as is otherwise the case after 30 minutes."

Bathing photographic prints after fixation in a 2% solution of Kodalk balanced alkali (sodium metaborate) was suggested by J. I. Crabtree[17] in 1950 for either manual or machine processing. The prints should be rinsed in water, squeegeed, or well drained before a 3- to 4-min immersion in the Kodalk bath. Each gallon of the Kodalk solution should be replaced after one hundred 8 × 10-in. double-weight prints or one hundred and fifty single-weight prints are treated.

These examples of the successful elimination of thiosulfate and silver thiosulfates from fixed photographic materials are the result of changing the pH of the gelatin of the emulsion layer. The thiosulfate and silver thiosulfate ions are bound strongly by the aluminum-gelatin complex that is formed during the fixing of emulsion layers in potassium alum fixing baths below the isoelectric point of gelatin. If the pH of the gelatin is raised much above its isoelectric point, the charged condition of the gelatin is changed from positive to negative. The aluminum hardener is removed from the gelatin and takes the mordanted thiosulfate and silver thiosulfates with it. (See Figure 6.) Aluminum hardening may also be removed by citric or similar acids that complex with the aluminum and remove it from the gelatin. Any bound thiosulfates that were held by the aluminum-gelatin complex are freed and then removed during the washing in water.

Alkaline solutions aid in the removal of thiosulfates from film negatives or paper prints, but the effectiveness varies with the alkali.[47] A direct comparison was made of distilled water, ammonium hydroxide, Kodalk, sodium hydroxide, and sodium carbonate solutions (0.3%) for 2 min following an

8-min wash after normal processing of film. The alkalis cut the time for washing by more than 50%. Ammonium hydroxide was the most effective alkali, and its alkaline solution had the least effect on the emulsion layer. The ammonium hydroxide solution was also most effective with paper prints in eliminating the adsorbed thiosulfates, again with little effect on the physical properties of the emulsion layer, but a washing time of 45 min was required.

The removal of the hardening of gelatin layers of films or prints can result in serious softening of the emulsion layer.[48] Almost all the hardening given to matrix film, whose emulsion layer is not hardened during manufacture, by an F-5 fixing bath was removed by a 5-min immersion in 2% solutions of sodium carbonate, sodium metaborate (Kodalk), or ammonium hydroxide. As a result, considerable swelling of the gelatin emulsion layer was produced by the alkaline baths or a 2% solution of sodium citrate.

Although effective for the elimination of the thiosulfates, alkaline solutions cause the loss of hardening from the emulsion layer, increasing the risk from

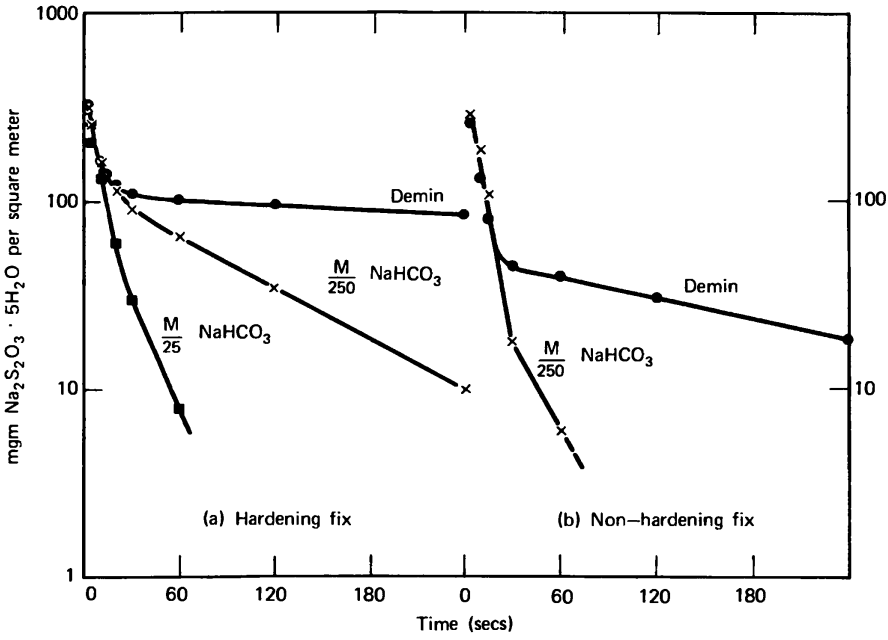

Figure 6. Residual thiosulfate is shown after fixing in (*a*) ammonium thiosulfate fixer with aluminum hardener and (*b*) a similar fixing solution without hardener, then washing in demineralized water or dilute solutions of sodium bicarbonate. The fast, negative film was bathed 4 min in a developer without the developing agent, rinsed 30 sec in demineralized water, fixed 5 min in either fixing bath (pH 4.35 for each), then washed in the demineralized water or bicarbonate solutions. [A. Green and G. I. P. Levenson, *J. Phot. Sci.*, 18: 1 (1970).]

abrasion or reticulation. The gelatin layer may be too soft to be pressed against a ferrotyping surface. When gelatin softening is obtained after bathing prints in an alkaline bath, immersion of the prints for 1 or 2 min in 2% formaldehyde solution will harden the emulsion layer sufficiently for the prints to be ferrotyped.

Oxidizing Baths for Conversion of Thiosulfates

Suggestions for the complete removal of thiosulfates from negatives and prints have ranged from washing only in water[49] ("use the only perfect eliminator, pure water")[50] or with a sodium thiosulfate solution itself[51] to a variety of chemical baths. One of the first proposals was made by F. W. Hart[52] in 1864. Prints were immersed in a solution of chlorine and barium chloride to convert any residual sodium thiosulfate into barium sulfate and sodium chloride. Silver thiosulfates were changed to sodium sulfate and silver sulfite. The silver sulfite, in the presence of the chlorine, would be converted to silver chloride, which was then solubilized with ammonia and washed away. Hart[53] claimed to have originated the name "hypo eliminator" for his solution for destroying residual thiosulfate and silver thiosulfates.

Hypo eliminators do not eliminate thiosulfates but rather convert them to other products. The objective of all hypo-eliminator solutions is to form innocuous, water-soluble compounds, such as sodium sulfate, from the thiosulfates. In many cases the oxidation of thiosulfate and silver thiosulfate may also produce compounds that are quite as unstable and deleterious as the thiosulfates might have been. Through the years, however, a large number of chemical preparations have continued to be proposed as hypo eliminators. A chronological history of these chemical treatments was compiled by J. I. Crabtree, G. T. Eaton, and L. E. Muehler,[47] as listed briefly at the top of page 659.

None of these chemical treatments was effective enough to give complete image permanence. Some of the compounds were successful in oxidizing the residual thiosulfate but only formed the tetrathionate, $S_4O_6^{2-}$, which is chemically unstable and causes image fading. Iodine, for example,[64] destroys thiosulfate

$$2Na_2S_2O_3 + 2I \longrightarrow 2NaI + Na_2S_4O_6$$

but the tetrathionate, $S_4O_6^{2-}$, is easily decomposed into trithionate, $S_3O_6^{2-}$, and sulfur, S. The trithionate is also unstable and decomposes with the release of sulfur.

Hypo eliminators used in acid solution have been ineffective in completely oxidizing the thiosulfates to inert, soluble reaction products. Early attempts to use alkaline ammonia–hydrogen peroxide solutions were not completely successful because some thionates were formed as well as the sulfate from the

Chemical	Year	Proposer
Hypochlorous acid	1864	F. W. Hart[52]
Hydrogen peroxide	1866	Angus Smith[54]
Sodium hypochlorite	1866	F. W. Hart[55]
Iodine	1872	H. W. Vogel[56]
Zinc hypochlorite	1881	L. Belitzski,[57] G. Scholik
Potassium persulfate	1894	Schering[50]
Potassium percarbonate	1901	G. Meyer[50]
Ammonium persulfate	1902	A. and L. Lumière,[58] A. Seyewetz
Alkaline perborates	1903	G. F. Jaubert[50]
Potassium permanganate	1904	I. Pearse[59]
Sodium-*p*-toluene sulfochloramide	1922	E. F. Shelberg[60]
Ferrous sulfate	1925	John Henry Watson[61]
Sodium hypochlorite plus sodium chloride	1931	R. Namias[62]
Hydrogen peroxide plus ammonia	1931	*Das Lichtbild*[63]

thiosulfate. According to Crabtree, Eaton, and Muehler,[47] some of these early failures were due to the use of neutral or insufficiently alkaline peroxide solution. These investigators found that "alkaline peroxide having a suitable pH value oxidizes the thiosulfate completely to sulfate."

Ammonia was found to be the most suitable alkali, as it volatilizes, leaving only the sodium and ammonium sulfates. The ammonia-peroxide solutions had to have a pH value of at least 9.8 to be satisfactory as hypo-eliminating solutions. Ten milliliters of 28 % ammonium hydroxide (ammonia) added to 125 ml hydrogen peroxide (3 %) and 875 ml water was an effective eliminator of the thiosulfate. A bath with greater exhaustion life was made by adding the 10 ml of the 28 % ammonium hydroxide to 500 ml hydrogen peroxide (3 %) and 500 ml water. These two hypo-eliminator solutions were designated Kodak HE-1 and HE-2[47]:

Kodak HE-1: Hypo-Eliminator Solution for Professional and Amateur Use

Water	500 ml
Hydrogen peroxide (3 % solution)	125 ml
Ammonia (3 % solution)	100 ml
Water to make	1 liter

To make 3% ammonia, dilute one part of 28% ammonia with nine parts of water.

Prepare HE-1 solution just before use, keep in open tray during use, then discard.

Wash the prints for about 30 min at 65 to 70°F in water running rapidly enough to replace the water in the container once every 5 min. Then immerse each print about 6 min at 70°F in the hypo-eliminator solution (Kodak HE-1), and wash about 10 min before drying.

Kodak HE-2: Hypo-Eliminator Solution for Commercial Photofinishing Use

Water	300 ml
Hydrogen peroxide (3% solution)	500 ml
Ammonia (3% solution)	100 ml
Water to make	1 liter

To make 3% ammonia, dilute one part of 28% ammonia with nine parts of water.

Note: Commercial hydrogen peroxide should be stored in a loosely stoppered bottle, or one with a boreglass tube in the stopper, away from light and heat.

Wash the prints for about 15 min at 65 to 70°F in water running rapidly enough to replace the water in the container once every 5 min. Then immerse each print for about 5 min in the hypo-eliminator solution (Kodak HE-2), and wash about 10 min before drying.

Any gelatin image on a waterproof support can be freed completely from the thiosulfates by washing in water without the use of a hypo eliminator. With photographic prints on paper base, however, washing, no matter how thorough, can never remove all the thiosulfates retained in the baryta layer (if present) or adsorbed by or held within the paper fibers of the base. For paper prints a hypo eliminator of the ammonia-peroxide type is necessary to achieve the optimum stability of the image.

Ammonia–hydrogen peroxide solutions may cause a slight change in tone of some prints, so the addition of 1 g potassium bromide to each liter of the hypo eliminator has been suggested to prevent the tone change. Such hypo-eliminator solutions were given in U. S. Patent 2,338,662 of Lowell Muehler. A slight yellowing of the white areas of prints may be minimized by bathing the prints for about 2 min in either a 1% acetic acid solution or a 1% sodium sulfite solution before the final washing.

These suggestions have been incorporated in the standard, ANSI PH4.32-1965,[65] for the evaluation of the level of stability of processed images on

black-and-white photographic papers. Following an acetic acid stop bath (96 ml of 28 % acetic acid in one liter of distilled water) and two-bath fixation (5 min each in fresh baths containing 250 g crystalline sodium thiosulfate in a liter of distilled water) the prints are washed with suitable agitation for 30 min in water flowing at a rate to fill the washing vessel once every 5 min. The prints are then bathed for 5 min in

PH4.32-1965 Hypo Eliminator

Distilled water	300 ml
Hydrogen peroxide (3 %)	500 ml
Ammonium hydroxide (28 %)	10 ml
Potassium bromide	1 g
Distilled water to make	1 liter

(This solution is prepared immediately before use, kept in an open container during use and then discarded. Do not store in a stoppered bottle or the bottle may be broken by the evolved gas.)

The prints are then transferred directly to a 1 % solution of sodium sulfite and agitated for 2 min. The final wash in running water is for 20 min, followed by air drying. All solutions and the wash water should be 68 ± 2°F.

In practice, it may be desired to use a dryer for drying the prints. The tendency of the treated prints to stick to the dryer was said to be prevented by bathing the prints before drying for 3 to 5 min in a 50 % denatured alcohol solution.[47] Ferrotyping surfaces must be kept clean, and excessive drying temperatures should be avoided.

An alkaline hydrogen peroxide hypo eliminator, such as HE-1, does not oxidize all of the thiosulfate present as a silver thiosulfate complex in the high densities of the image. Chester I. Pope[40] found that the adsorbed silver thiosulfate complex ions could be oxidized by the ammonia-peroxide solution if sodium chloride, potassium bromide, or potassium iodide were present in the same solution. The bromide, chloride, or iodide ions were equally effective in the proportions of 8 g sodium chloride, 0.8 g potassium iodide, or 0.5 g potassium bromide.

The mechanism of the reaction is thought to be similar to that of sodium chloride in sea water. The halide ion reacts with the adsorbed silver thiosulfate complex, releasing the thiosulfate ion and forming silver halide. The thiosulfate is oxidized by the peroxide to the water-soluble sulfate ion. The silver halide is solubilized in the excess halide ions and removed from the photographic material.

The action of various fixing baths is summarized in Table 5.

Table 5. Removal of Thiosulfate and Silver Thiosulfate Ions from Processed Photographic Film and Paper

Type of Fixing Bath	Mordanted Ion	Means of Removal
	Film	
	Potassium Alum Baths (F-5, F-10)	
(a) Fresh	$S_2O_3^{2-}$	1. Increase temperature of wash water or agitation of wash water 2. Increase pH of fixing bath to value above the isoelectric point of gelatin; for example, use F-6 3. Use dilute ammonia solution (0.03%) or 2% sodium metaborate rinse 4. Use hypo clearing compound before washing, such as 1% sodium sulfite
(b) Exhausted	$[Ag_x(S_2O_3)_y^{n-}]$	1. Increase pH above isoelectric point; for example, use F-6 2. Use any second or third fixing bath
	$S_2O_3^{2-}$	1. Use a second fixing bath with pH above isoelectric point, such as F-6 2. Use a second fixing bath minus potassium alum
	Chrome Alum Baths (F-16, F-23)	
(a) Fresh	None	
(b) Exhausted	$[Ag_x(S_2O_3)_y^{n-}]$	1. Increase pH of bath to value above 5.0 (no hardening at this value) 2. Use a second or third fixing bath; use chrome alum or F-24

Table 5. ***(continued)***

Type of Fixing Bath	Mordanted Ion	Means of Removal
	Paper	
	Bisulfite Fixing Bath (F-24)	
(a) Fresh	$S_2O_3^{2-}$	1. Increase temperature of wash water 2. Increase agitation of prints in water 3. Use 1% sodium sulfite or 2% sodium metaborate before washing 4. Use peroxide-ammonia hypo eliminator
(b) Exhausted	$[Ag_x(S_2O_3)_y^{n-}]$	1. Any second or third fixing bath followed by 2. Hypo eliminator
	Chrome Alum Baths	
	As with F-24	As with F-24
	Potassium Alum Baths	
(a) Fresh (b) Exhausted	As with F-24 but much greater quantities	As with F-24

Source: Based on a table from J. I. Crabtree, G. T. Eaton, and L. E. Muehler, *J. SMPE*, **41**: 44 (1943).

WASHING

Washing is a procedure of using water to dilute the thiosulfate content of a photographic material to a sufficiently low level so that the silver image has an "adequate" storage life. Each 1000 sq ft of fixed film carries about $\frac{1}{3}$ gal of fixer (330 g thiosulfate) into the wash water. After washing to a thiosulfate content of 0.05 mg/sq in., G. I. P. Levenson[66] estimated that the residual

water in positive film, after washing and squeegeeing, will still contain a concentration of at least 4 g thiosulfate per liter of absorbed water. Negative film emulsions just before drying can carry a thiosulfate solution of 10 g/liter. Thus, the levels of permissible thiosulfate set for commercial expediency by J. I. Crabtree, G. T. Eaton, and L. E. Muehler[6] still allow a large amount of thiosulfate to be retained after washing and drying.

Washing involves three steps: (1) diffusion of the salts within the emulsion to the emulsion surface, (2) removal of the salts from the surface by water, and (3) renewal of fresh water at the surface. Early studies by A. Vincent Elsden[4] and A. W. Warwick,[67] and later by K. C. D. Hickman and D. A. Spencer,[5] have shown that the thiosulfate leaves the film emulsion layer exponentially down to extremely low levels (the limit was estimated to be about 2 to 30 ppm in the swollen gelatin). The exponential rate of removal means that the quantity of thiosulfate leaving at any moment is proportional to the quantity still present in the emulsion layer.[32] It will take exactly the same time, regardless of the level of the thiosulfate in the emulsion layer, for one-half of the thiosulfate to diffuse away. If 50% of the thiosulfate is removed in the first minute, 50% of the remaining 50% (or 25% of the original amount) will be removed in the next minute, and 50% of the remaining 25% (or 12.5%) will be removed in the next minute, and so on.

This exponential rate of removal of the thiosulfate from the swollen emulsion layer is dependent upon conditions where the supply of water at the emulsion surface is ideal; that is, fresh water is continuously being supplied and thiosulfate-containing water is continuously being removed. This condition is probably achieved only when a vigorous jet of water scrubs the film surface violently. Under more moderate conditions the thiosulfate and other salts diffuse from a region where the salt concentration is high (the emulsion layer) to a region where it is lower (the wash water).

If the layer of water at the emulsion surface is not replaced quickly, the salt concentration will increase in this water layer and the force compelling the salts to leave the emulsion will decrease, thus reducing the rate of removal of the salts from the emulsion. To insure that the surface layer of water always has a low salt concentration, it is necessary to provide either (1) a flow of water with a high degree of agitation or (2) a complete removal of the water and a replacement with a fresh volume of water. Practical washing is concerned with these two conditions: vigorously applied flowing water minimizes the time of treatment; small volumes of water applied separately minimize the total volume of water needed but take longer.

During washing the rate of diffusion of the salts within the emulsion to the surface is beyond human influence. It is the removal of the salts once they reach the surface that may be controlled by the method of application of the wash water. Increasing the flow beyond a certain maximum rate, however,

does not increase the elimination of the salts within the emulsion. A graphic analogy was given by K. C. D. Hickman and D. A. Spencer[68]: "The diffusion of salt molecules from an emulsion into a stream of water may be compared to the passage of people through a station barrier on to a platform, whence a series of trains will remove them to their destinations. The booking office will represent the material, the surface of which is the barrier. The passengers on the platform correspond to the viscous layer of freshly diffused salt, and the trains the stream of water by which it is ultimately removed. If the train accommodation is inadequate, the crowd collecting on the platform will obstruct those issuing from the barrier and the rate of passenger removal will be diminished. On the other hand, increasing the number of trains beyond a certain limit will not increase the numbers passing the barrier; the trains will merely go away half empty."

The washing of photographic papers departs from the near-ideal elimination of the thiosulfate and other salts from a film emulsion layer. At first the rate of removal of the salts is rapid, but there follows a considerable period during which a sluggishly diffusing substance is extracted slowly from the paper prints. Thiosulfates are removed quite readily from the gelatin emulsion layer, as with film emulsion layers, but the lag in removal of thiosulfates from paper prints is due to the properties of the fibrous paper sheet (and the baryta layer, if present).

This slow removal of thiosulfates was described by Hickman and Spencer[68] as follows: "Immersion in the strong hypo will fill the majority of pores and fibers with salt, which will come away completely on washing. The protected pores and fibers will take up varying small amounts of the strong hypo which they will give up equally slowly when the concentration in their neighbours has fallen below their own value. The effusion of salt, rapid at first, will become extremely slow in the later stages."

Any treatment that causes the emulsion layer of film or plates to swell increases the diffusion path within the emulsion and may retard slightly the washing of the emulsion free of thiosulfates or other salts. The same treatment, however, would be beneficial to the washing of paper prints. The paper emulsion layer would swell and impede slightly the washing of the emulsion layer, but most of the washing time is concerned with the elimination of the thiosulfate from the rest (baryta layer or paper base) of the paper print. A treatment, such as with an alkaline solution, that causes the paper fibers to hydrate and swell, or to rupture the paper sizing, will leave the paper fiber surfaces and channels more accessible to washing by water. If the water can penetrate to where the thiosulfate is held, strong osmotic forces will compel the thiosulfate to leave the region of greater concentration in or on the fibers for the lesser concentration of thiosulfate in the wash water. One estimate of this osmotic pressure expelling the thiosulfate was of the order of 15 kg/cm^2.[69]

The use of strong salt solution before washing involves the reverse of this osmotic force (desorption): The salt is compelled to enter through the pores of the fibers and penetrate the channels between fibers, displacing the thiosulfate into the solution. The salt solution is then washed out with water during the final washing step.

Importance of Water Temperature, pH, and Purity

The temperature of the wash water is a factor in the elimination of the thiosulfates, especially from paper prints. A value of 2.3 times faster for a 10°C (18°F) rise in wash water temperature has been reported.[69] Relatively unhardened emulsions may swell excessively at high temperatures, and the increased diffusion path may inhibit the removal of thiosulfates from film emulsions. Such film products should be washed in water between the temperatures of 40 and 80°F, preferably at the same temperature as the developer, usually 68 to 75°F. The washing at 80°F is 30% faster than at 40°F to remove all the thiosulfates. Specially hardened thin-emulsion photographic films have been designed to be processed above 85°F, and they wash very rapidly in water at the high temperatures. With photographic papers thiosulfate is extracted more quickly from the paper fibers when warm water (70 to 75°F) is used rather than cold water. The washing time for photographic papers should be increased if the wash water temperature falls below 65°F.[70]

Swelling of the gelatin layers of a photographic material allows the adsorption of considerable amounts of water that must be removed during drying. A photographic film layer may be 10 μ thick when dry, 37 μ after development, 60 μ after fixation, and 85 μ after washing. These figures are from U. S. Patent 3,467,519, which proposes to use a deswelling bath after washing in order to reduce this swelling to near the original thickness of the dry film layer. Reduction of the emulsion thickness permits rapid drying. Three minutes immersion in a solution containing 20 g glacial acetic acid and 10 g naphthol-sulfonic acid-7 reduced layer swelling from 85 to 15 μ. Other straight chain or ring compounds (five or more carbon atoms) containing sulfonic acid or sulfate groups are effective deswelling agents. An alkaline bath, such as 4% sodium carbonate solution, will within 1 min cause the deswelling to be removed, indicating the reversibility of the treatment with the sulfonic acid solution.

As previously indicated, pure water makes a poor washing medium. Hard water with dissolved salts, especially bicarbonates, or soft water with sodium bicarbonate present at a fraction of a gram per liter, is superior to pure water in washing power, especially after fixing with an acid hardening bath con-

taining potassium alum. Chlorinated water has been claimed to have some thiosulfate-eliminating action.[71] Water for washing may contain mineral matter (sand or rust, for example), vegetable matter (wood particles), sulfurous gases, or other undesirable impurities. Wash water should be filtered to remove any particulate matter that might adhere to a soft gelatin emulsion layer, especially small-size film negatives or color materials. Dissolved sulfide gases may be removed by boiling the water. In this era of increasing pollution of water supplies, the suitability of water for washing should be carefully assessed and assumptions of purity should be avoided.

D. K. Allison[72] suggested that both the fixing bath and the wash water should be adjusted to the pH of the isoelectric point of gelatin. He stated that the amount of water carried in the gelatin "passes through a sharp minimum in the neighborhood of pH 4.8, and that film washed at this pH contains only three-fourths as much water as at the usual pH 8.1. Smaller water absorption would mean more rapid drying, resulting in a claimed three- to fourfold increase in the drying rate."

These claims have been disputed by S. E. Sheppard and R. C. Houck,[73] who found that, with an acid hardening fixing bath, it was a disadvantage to wash at the gelatin isoelectric point (around pH 4.9) rather than at pH 7 to 8. The time to remove the thiosulfates from the gelatin layer was increased. Less water was not retained by the gelatin. Only with a nonhardening fixing bath did washing time with water at the isoelectric pH remain about the same while less water was adsorbed by the gelatin, shortening the drying time.

Design of Practical Washing Systems

Satisfactory washing to commercial standards is attained while the photographic material still carries a fairly high concentration of thiosulfates. G. I. P. Levenson[66] has stated, "It is clear that, in general, satisfactory washing can be achieved merely by a hundred-fold dilution of the fixer left in the emulsion after fixation. For example, the film leaving the fixer carries a thiosulfate solution of about 30 percent concentration. If this is diluted one-hundred-fold to 0.3 percent, the film would meet the commercial requirements even for motion picture positive films."

Suitable dilution of the adsorbed thiosulfates during practical washing usually involves either of two types of treatment: (1) immersion in a volume of water for a time period before the water is completely changed for a new volume of water, or (2) the use of water flowing past the surfaces of the photographic material. This flowing water may be recirculated within the washing vessel, or fresh water may flow only once past the film or paper surface.

Separate volumes of water may be used for washing in photographic darkrooms where water is in short supply. Running water is generally used in darkrooms or in processing machines where an adequate supply of suitable water is available.

For efficient washing of photographic materials a complete change of water in the vessel should be made every five minutes. This time is sufficient for the concentration of the thiosulfate in the photographic material to reach a practical equilibrium with the concentration of the thiosulfate that has diffused into the wash water from the material. A longer time would result in only slightly more thiosulfate diffusing from the film or paper into the water. Five or six 5-min changes of water are sufficient to insure permanence of images on film or glass supports. The reverse equilibrium can also occur. If a freshly fixed film is introduced into a volume of water containing partly washed photographic materials, the concentration of the thiosulfates in the water will be greater than the concentration of the thiosulfates in the photographic materials. In this case, thiosulfate will be adsorbed by the gelatin and paper base, increasing the time to wash. Washing time should be measured from the last addition of fixed photographic materials.

Thiosulfate-laden water is heavier than fresh water and will settle to the bottom of the washing tank or tray in the absence of agitation.[74] Photographic materials should be washed emulsion down[75] or vertically to allow the thiosulfate-containing water to escape most easily. Often, washing containers are designed to allow some extra space at the bottom for the thiosulfate-water to accumulate, such as in the almost stagnant washing involving separate changes of water.

Water must be able to reach all surfaces of the photographic material for efficient removal of the thiosulfates and other salts. The water tray or tank, however, should not be any larger than is necessary to accomplish this objective. Very large containers are inefficient and wasteful of water. Agitation of the water during the wash period greatly shortens the washing time, as the contaminated water on the surface of the photographic material is quickly replaced with fresh water.

An efficiently designed washing system begins with a removal of the processing solution, such as a fixing bath, from both surfaces of a film or paper before the photographic material enters the wash water. Rubber wiper blades, polyurethane squeegees, wringers, rotary buffers, or air knives can greatly cut down on the carryover of processing solutions into the washing system. Careful and regular maintenance is necessary to avoid emulsion damage. The mechanical elimination of thiosulfate by squeegeeing does not minimize the need for washing but does reduce the amount of water necessary to secure adequate washing.[76,77]

The most efficiently designed washing systems use water flow and water

direction to sweep the photographic material and the washing vessel free of contaminated water. K. C. D. Hickman[78] stated, "*The first seven minutes is spent in washing the film—the rest of the time in washing the tank.* The ideal to be aimed at is quite clear. We must design a vessel and water-changing system of such a nature that the tank washing races the film washing. As soon as the hypo has left the emulsion, it must be made to leave the tank."

The design of washing systems often achieves good tank washing by introducing the water at the bottom of the tank and having the overflow at the top. The water from the tap should be made to flow down the center of a small film tank to the bottom and then leave the tank by the pouring exits at the top edge. In this way hypo-laden water is flushed from the tank and replaced with fresh water. With small tanks used for washing sheet films, the introduction of the water at the bottom also removes contaminated water from the tank. A tray siphon used for washing prints flows water over the print surfaces at the top of the vessel and siphons hypo-laden water from the bottom of the tray.

The design of washing tanks for continuous processing often uses several tanks with a countercurrent or cascade flow of water. Fresh water enters the last tank, flows from that tank to the next through any others to the first tank. The direction of flow of water is counter to the direction of travel of the photographic material. As the film or paper moves forward it enters tanks that have water less contaminated with thiosulfates. The final water tank rinses the photographic material in water having a low concentration of thiosulfate salts. Calculations of water flow rates in immersion washing have indicated that efficient washing is most likely to be carried out in a cascade system involving several small wash tanks rather than in a single large washing tank.[79]

Because the application of water as well as the rate of water flow is involved, a wondrous array of washing equipment has been designed to achieve maximum washing with minimum water and minimum time. The design of washing devices was studied early by K. C. D. Hickman and D. A. Spencer[80] and has been the subject of critical research into new systems since then. Achieving turbulent flow at the surface of photographic materials is often the object of equipment design to shorten treatment times.[81] Water sprayed from jets, according to C. E. Ives,[82] can cause the washing time to be "reduced by a factor of 50 by continuous highly effective renewal of the water at the emulsion surface as compared with ordinary immersion techniques in which agitation is poor and turnover in the tank is slow. This is achieved, for example, by continuous forceful spraying of the entire surface with fresh water."

Gaseous-burst agitation—that is, the introduction of air or nitrogen gas in bursts through holes in pipes at the bottom of the wash tank to form bubbles

that rise—has been described by J. A. Smibert and M. O'Bern.[83] Air bubbles have also been introduced into the water line by a water-driven air suction pump.[84] This aerated water is introduced through holes in pipes at the bottom of a washing tank for photographic prints. The residual thiosulfate in photographic prints was said to be reduced below normally accepted limits with a 30-min wash with economical use of water.

Efficient removal of thiosulfates is important with color processing.[85] Both the thiosulfate and water will be carried over into the stabilizing bath following the water wash. The stabilizing bath becomes ineffective when diluted with contaminated hypo-laden water, resulting in a green color balance.

METHODS FOR TESTING FOR RESIDUAL THIOSULFATES

The level of residual thiosulfate contained in the photographic material is a primary factor in the stability of photographic images upon storage. J. Pouradier et al.[86] found "that the stability of photographic images on paper depends primarily on the storage conditions and the level of residual thiosulfate." The effectiveness of the washing may be best judged by testing for the residual thiosulfates still retained in the photographic material after the washing step.

According to American National Standard PH1.28-1969,[15] the maximum permissible concentration of residual thiosulfate for archival keeping of silver-gelatin photographic films on cellulose ester base is 0.006 mg/sq in. for fine-grain copying, duplicating, and printing films (including microfilm) and 0.018 mg/sq in. for medium-grain continuous-tone camera films and coarse-grain X-ray films. The residual thiosulfate is expressed as anhydrous sodium thiosulfate. If washing is efficient enough to remove the residual thiosulfate and thionates to the level specified, it is believed that the film will be adequate for archival record purposes when stored under controlled conditions.

Chemical reagents have been used to measure the thiosulfate content of wash water or the water drippings collected from the photographic film or print when withdrawn from the wash water. The thiosulfate content of the wash water may be measured by electrical apparatus, as water containing thiosulfate ions has a higher electrical conductivity than water without them. Alternatively, a washed film or print may be bathed in a definite volume of a chemical test solution, or a known volume of the test solution may be applied to a definite area of the surface of the film or print. In some test procedures a drop of the test solution on the surface, without regard to volume or area, is sufficient to produce a color that is related to the concentration of the retained thiosulfate.

Chemical Test for Thiosulfates in the Wash Water

The four chemical tests described below are the ones most commonly used for measuring the thiosulfate content of the wash water or drippings from film or prints.

1. *Iodide-starch or iodide-azide-starch test.*[87,88,89] The test solution contains 0.6% soluble starch and 0.13% each of iodine, potassium iodide, and sodium azide. Two milliliters of this solution is diluted to about 200 ml with water. The wash water from film, plates, or prints is allowed to drip into the solution. An immediate color change, from blue to colorless, indicates inadequate washing. If the color is not discharged in a few seconds, the washing is regarded as satisfactory.

2. *Silver nitrate test.* In the presence of excess silver ions, sodium thiosulfate reacts with silver nitrate quantitatively to produce brown silver sulfide:

$$2AgNO_3 + Na_2S_2O_3 + HOH \longrightarrow Ag_2S + 2NaNO_3 + H_2SO_4$$

This test was used in 1902 by Lumière and Seyewetz[58] to test for thiosulfate in the wash water. A 1% solution of silver nitrate made acid with acetic acid (2%) or sulfuric acid (0.5%) will help convert any sulfite to bisulfite and neutralize the alkali, if present. Any ions, such as sulfite, or alkaline substances will reduce the concentration of silver ions and interfere with the results. The addition of large quantities of thiosulfate ions will also give inaccurate results.

3. *Kodak hypo test HT-1a.* Probably the best-known test solution for making a drip test from the wash water is the Kodak hypo test solution HT-1a:[90]

Distilled water	180.0 ml
Potassium permanganate	0.3 g
Sodium hydroxide	0.6 g
Water (distilled) to make	250.0 ml

To make the test with film take 250 ml of distilled water in a clear glass container and add 1 ml of the alkaline permanganate solution (HT-1a).

Take the film from the wash water and allow the water from it to drip for 30 sec into the test solution. If a small amount of thiosulfate is present, the violet color will slowly turn to orange in about 30 sec; with a larger amount of thiosulfate present, the orange color will change to yellow. The orange or yellow color of the test solution indicates that the film should be returned to the wash water. Washing should be continued until further testing produces no change in the violet color.

To make the test with prints take 125 ml of distilled water in a glass container and add 1 ml of the HT-1a solution. Pour 15 ml of this diluted solution into another clear glass container.

Then take six prints, size 4 × 5 in. or equivalent, from the wash water and allow the water from them to drip for 30 sec into the 15 ml of the dilute test solution. If a small quantity of hypo is present, the violet color will turn orange in about 30 sec and become colorless in 1 min. In either case the prints should be returned to the wash water and allowed to remain until further tests show that the hypo content has been reduced to a safe margin.

4. *Mercuric chloride test.*[91] This test can be adapted to testing wash water or the drippings from the water adhering to the surface of a photographic material. The test solution consists of 25 g mercuric chloride and 25 g potassium bromide in one liter of water. The addition of 10 ml of this solution to the water sample produces a turbidity in the water if thiosulfate is present. This turbidity is then compared with the turbidity in solutions that contain known amounts of thiosulfate, using a visual or instrumental method of comparison.

Drip testing is attractive as a method of measuring the thiosulfate present because the photographic material is not harmed, but, as has been pointed out,[90] "the hypo determined represents neither the hypo content of the wash water nor of the material. The drippings actually contain more hypo than the wash water because of diffusion of hypo solution from within the film or print during the drainage period and, therefore, they contain some of the hypo from within the material. This type of test, however, when made under controlled conditions, gives a better indication of the residual hypo content of the material than a test made with the wash water."

The presence of sulfite or alkalis will interfere with the iodine-azide-starch or silver nitrate tests. Sulfites or organic impurities in the wash water interfere with the permanganate test. The mercuric chloride test is highly specific to thiosulfate, but this test is more appropriately applied to the thiosulfate in the photographic material itself. Even when a valid test of the wash water or drippings from the film or prints indicates the complete absence of thiosulfate, the film and especially photographic paper prints may still retain considerable residual thiosulfate. *Tests for thiosulfate in the wash water may be used for rough control of the washing process, but quantitative estimation of residual thiosulfate in the photographic material is not possible.*

Chemical Tests for Thiosulfate in Photographic Materials

The stability of photographic images is largely determined by the residual thiosulfates present in the photographic material. Current belief holds that the photographic film or print, not the wash water, should be tested for total

residual thiosulfates. The use of permanganate, iodide-starch, or iodide-azide-starch solutions for spotting or bathing tests has not proved to be as successful as the mercuric chloride–potassium bromide test solution. This test method, first proposed in 1930 by J. I. Crabtree and J. F. Ross,[91] now forms the basis of ASA Standard PH4.8–1958, "Method for Determining the Thiosulfate Content of Processed Black-and-White Photographic Film and Plates."[92]

The ASA Standard Method outlines the test as follows:

> The test depends upon the production of a degree of turbidity or opalescence in the test solution which is related to the amount of thiosulfate present in the sample. A measured area of the sample is immersed for a sufficient time in a given volume of the test solution. At essentially the same time as the sample is immersed, comparison solutions are prepared by adding known quantities of thiosulfate solution of specified concentration to the required volumes of the test solution. When thiosulfate is present, a precipitate is formed which rises to the upper part of the test solution. After standing undisturbed for a given period of time, the tubes are agitated to distribute the precipitates uniformly. The turbidity of the sample tube is compared with the turbidity of the comparison tubes and matching turbidities are found. Since the quantity of thiosulfate in any comparison solution is known, the amount in the sample is thus quantitatively determined.

The mercuric chloride–potassium bromide test solution is very sensitive to the presence of thiosulfate, being able to detect 1 mg of thiosulfate per square inch of a black-and-white film or plate material. The test is not intended for color photographic materials. Sulfite, bisulfite, or thionates, such as trithionate and tetrathionate, are not detected. Residual thiosulfates in photographic materials decompose rather quickly into thionates after processing. The test for thiosulfates must be run within 24 hr or undetected substances will form that have a deleterious action on the stability of the processed image.

The Crabtree-Ross Method used in PH4.8-1958 has been the subject of considerable effort to overcome its known shortcomings. Residual thiosulfate is converted to trithionates in a few weeks and into tetrathionates after two or three months. These compounds have been shown to be dangerous fading agents for the silver image, yet their presence is undetected by the testing procedure.[93] The error in the estimation may be as large as 100% with aged film samples.

The Crabtree-Ross method depends upon the reaction of any thiosulfate present in the emulsion with the test solution to form mercurous bromide, which produces a turbid solution. This method has been criticized by C. I. Pope[94] as failing to measure all the thiosulfate present, because some turbidity is formed within the photographic material rather than in the solution,

giving results that are too low. Also some silver is reported as thiosulfate. The silver image of the film or plate sample turns white because of the reaction

$$2Ag + 2HgX_2 \longrightarrow 2AgX + Hg_2X_2$$

where X is either chloride or bromide. Some of this precipitate due to silver goes into the test solution and influences the results. The turbidity produced in the standard solutions results from particles that are larger than those formed in the presence of the film sample. Gelatin dissolved from the photographic material during the test has an effect on the turbidity. A turbidity-reading error of no more than 10% has been estimated. The test sample of the photographic material is often taken from a clear area of the processed film or plate, yet it has been observed that areas of high image density may have as much as five times the residual thiosulfate, as determined by the Crabtree-Ross method, as clear film areas of the same film specimen.

One suggestion for improvement has been to use a technique to extract the thiosulfate from the film or plate sample with a bromide solution prior to the precipitating reaction. Gelatin has been added to the reagent to minimize differences in color and particle size. Then the comparison is made with a nephelometer, an instrument designed to compare turbidities. Polythionates are not detected, however.

Another variation in the testing technique extracts the retained thiosulfate from the film sample with a buffered solution of iodide and sulfite.[95] The iodide elutes the adsorbed compounds such as thiosulfates and thionates, and the sulfite reacts with tetrathionate and polythionates to re-form thiosulfate; unfortunately, however, trithionates are not measured by this method. The excess sulfite is then combined with formalin. Iodine is then added with a fractionated starch indicator, the iodine reacting according to

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

Any iodine that does react with the thiosulfate forms a blue color with the starch indicator. This color is then compared with that of thiosulfate standard solutions.

A new test method was proposed by C. D. Warburton and E. P. Przybylowicz[96] to replace the Crabtree-Ross test, which has encountered serious criticism. The residual thiosulfate is extracted from a 2-in.-square sample of the processed film by treatment with potassium iodide, then sodium borohydride is added to reduce the thiosulfate to sulfide. The sulfide formed by the reduction of the thiosulfate was then measured by a method based on the formation of methylene blue. A visual comparison method with known thiosulfate standards, or instrumentally with a spectrophotometer, may be used to determine the residual thiosulfate of the processed film. Although the method does not normally detect tri- and tetrathionate, it may be adapted to

analyze for thiosulfate, trithionate, and tetrathionates in one solution. The sensitivity of the test is said to be seven times greater than that of the PH4.8-1958 testing procedure based on the Crabtree-Ross turbidimetric test. Another test method, the Silver-Ion Demand method (SID), involving a titration, has been proposed. This method is relatively insensitive to the time lapse between processing and running the test.[97]

Residual Thiosulfates and Thionates in Processed Photographic Papers

The Silver Nitrate Test

This test procedure, unlike the Crabtree-Ross and other similar tests, is dependent upon the conversion of residual thiosulfate within the photographic material to colored silver sulfide, according to the reaction

$$2AgNO_3 + Na_2S_2O_3 + H_2O \longrightarrow Ag_2S + 2NaNO_3 + H_2SO_4$$

The paper base of photographic prints, as well as the emulsion layer, contains residual thiosulfates, so it is most suitable to bathe the paper print in the test solution so the silver nitrate may reach all the thiosulfate. Although rapid and convenient, spot testing of the silver nitrate on the surface may give variable results because the water content of the wet print influences the extent of the diffusion of the silver nitrate solution. With either spotting or bathing, the photographic material is made useless. Silver nitrate solutions strongly stain human skin and care must be exercised in their use.

A drop of silver nitrate solution was placed on a washed print by A. and L. Lumière and A. Seyewetz[98] in 1908 as a test for retained thiosulfates. If the spotted area of the print did not darken within 2 to 3 min, the print was considered to be adequately washed. This technique was improved by E. Weyde in 1935 by soaking the print 1 to 3 min in a 1% solution of silver nitrate. The residual thiosulfate was converted in situ to silver sulfide. The color of the silver sulfide was fixed by washing the print briefly in water, treating for a short time in 5% solution of sodium chloride, fixing in a fixing bath, and washing again in water. The brown color, as viewed by transmitted light, was a measure of the quantity of the thiosulfate retained by the print. No color was observed when the thiosulfate content of the print was below 0.006 mg thiosulfate per square inch.

A silver nitrate test for residual thiosulfate in photographic prints was proposed in 1940 by J. I. Crabtree, G. T. Eaton, and L. E. Muehler.[47] An unexposed, white sheet of photographic paper (similar in weight and size to the regular prints) was processed and washed with the regular prints. A strip of this sheet was cut off, immersed for 3 min in a 1% silver nitrate solution, rinsed in water, and compared, while wet, with the wet, untreated portion.

No color difference should have been noticeable if thiosulfate was absent; a yellow-brown tint indicated the presence of thiosulfate.

This technique is essentially used for the Kodak hypo test solution, HT-2.[99] The excess surface water is wiped from the emulsion of an unexposed piece of photographic paper processed with the other prints. One drop of the following solution

Kodak HT-2 Solution

Water	750.0 ml
Acetic acid, 28%	125.0 ml
Silver nitrate	7.5 g
Water to make	1.0 liter

is placed on the emulsion surface of the print, allowed to stand for 2 min, rinsed with water to remove the excess test solution, and then compared with a commercially available (Kodak hypo estimator)[100] series of color patches that indicate residual thiosulfate quantities remaining in the print. If washing aids have been used, such as salt solutions, it is more accurate to immerse the entire print or sample in the silver nitrate test solution and then measure the transmission density. The HT-2 solution may also be used to test the degree of washing of films by using the spot-test or total-immersion techniques.[101]

All of the residual thiosulfates and thionates retained in a photographic material are converted by immersion in silver nitrate solution into a quantity of silver sulfide that is directly proportional to the thiosulfate and thionates present, as shown in the following reactions:

$$2Ag^+ + S_2O_3^{2-} + H_2O \longrightarrow Ag_2S + SO_4^{2-} + 2H^+$$

$$2Ag^+ + S_3O_6^{2-} + 2H_2O \longrightarrow Ag_2S + 2SO_4^{2-} + 4H^+$$

$$14Ag^+ + 4S_4O_6^{2-} + 12H_2O \longrightarrow 7Ag_2S + 9SO_4^{2-} + 24H^+$$

The intensity of the stain increases in direct proportion to the sulfide produced. Thus, the transmission density of a treated print would serve as an indication of the thiosulfate and thionates retained by the print after washing.

A procedure for the quantitative determination of residual thiosulfate in prints was proposed by J. I. Crabtree, G. T. Eaton, and L. E. Muehler[102] in 1943, using a three-solution immersion treatment. In the first solution the residual thiosulfate and thionates react with the silver nitrate to form silver sulfide in situ. In the second solution the excess silver nitrate is reacted with sodium chloride to form silver chloride, which is dissolved by the sodium thiosulfate of the third solution. The excess silver nitrate must be removed

because it darkens upon exposure to air and light. This additional coloration would interfere with the transmission-density reading made on the treated and untreated print samples. The difference of these densities is the density of the silver sulfide, which is proportional to the amount of thiosulfate in the print. The exact quantity of thiosulfate is obtained from a standard curve relating the density of the silver sulfide to the concentration of thiosulfate.

This silver nitrate test, slightly modified, is the basis of PH4.30-1962, "American Standard Method for Determining Residual Thiosulfate and Thionates in Processed Photographic Papers."[103] This test is said to be able to detect quantities of thiosulfate, measured as anhydrous sodium thiosulfate, as low as 0.003 mg/sq in. in photographic prints.

Three solutions are necessary for the PH4.30-1962 test:

Solution A

Distilled water	750.0 ml
Acetic acid (glacial)	30.0 ml
Silver nitrate	10.0 g
Distilled water to make	1.0 liter

Store this solution in a brown or dark-colored glass-stoppered glass bottle protected from strong light. Avoid contact of the solution with the skin.

Solution B

Distilled water	750.0 ml
Sodium chloride	45.0 g
Distilled water to make	1.0 liter

Solution C

Distilled water	750.0 ml
Sodium sulfite, anhydrous	15.0 g
Sodium thiosulfate, crystals	45.0 g
Distilled water to make	1.0 liter

The test procedure is described as follows: "A sample at least $\frac{1}{4} \times 1$ inch in size with a uniform minimum reflection density, preferably below 0.10, is removed from the print. One-half of the sample is dipped and allowed to remain submerged, with occasional agitation, in an excess of Solution A for four minutes. The sample is then totally immersed in Solution B for four

minutes and then in Solution C for four minutes, washed five to ten minutes in running water, and dried."[103]

The transmission densities of corresponding samples of treated and untreated prints are measured by a visual densitometer with a Kodak Wratten filter, No. 44, in the eyepiece or by a photoelectric transmission densitometer with Kodak Wratten filters, Nos. 44 and 38A, between the light source and the photocell. The difference of the density readings of the treated and untreated samples is the transmission density of the silver sulfide formed. The corresponding anhydrous sodium thiosulfate content of the print is then obtained by reference to the standard curve.

The silver nitrate test of PH4.80-1962 has been reported[104] to be time dependent when applied to double-weight prints. The silver nitrate penetrates or reacts very slowly with the residual thiosulfate. Extending the time in each solution from 4 to 30 min improved results without changing the normal manipulations of the standard test procedure. The covering power of the silver sulfide formed depends upon the structure of the paper, introducing errors which may indicate from one-half to two times the true amount of residual thiosulfate present. Some of the silver nitrate becomes adsorbed on the paper fibers or in the baryta layer. Later, this darkens and contributes density to the final densitometer reading and causes error.

Because of the serious questions about the validity of the Crabtree-Ross method for determining the amount of residual thiosulfate in film, efforts have been made to adapt the silver nitrate test for quantitative use with film materials. Acidic silver nitrate reacts with thiosulfates and thionates, yielding a silver sulfide stain that is proportional to the retained thiosulfates and thionates. With washed film this sulfide stain may be very weak, making a determination difficult. A spot-test method of determining thiosulfate down to 5 μg/sq in. has been proposed,[105] which uses four thicknesses of film and bleaches out the residual sensitizing dye. The three test solutions of PH4.30-1962 are used. This proposal was simplified further by C. I. Pope[106] for testing residual thiosulfate and thionates in microfilm. One solution and one wash step were eliminated by using a solution of ammonium hydroxide and sodium chloride to remove the excess silver ion after the silver nitrate treatment. The time required for the test was reduced to one-half that of the three-solution procedure.

Color photographic materials are not recommended for archival keeping. Dye stability, especially that of the magenta, appears to be related to the residual thiosulfate level, and exceeding recommended levels generally results in dye fading. Thus, tests for residual thiosulfate, such as the silver nitrate test[97] or the methylene blue dye test of C. D. Warburton and E. P. Przybylowicz,[96] can be used to gain information concerning the keeping properties of color photographic materials.

METHODS FOR TESTING FOR RESIDUAL SILVER

At present, the safe maximum quantity of residual silver compounds and silver complexes is not known for the archival keeping of photographic materials. It is known, however, that the silver ions remaining from inadequate fixation or the silver ions from the residual silver thiosulfates can combine with sulfur from the decomposition of residual thiosulfates or sulfur from atmospheric gases to produce silver sulfide in the photographic material. This silver sulfide forms a yellow stain most evident in the margins and the highlight areas of films and prints. A uniform yellow stain is probably more objectionable in a print than in a film, but the formation of silver sulfide should be avoided by satisfactory processing methods.

Two-bath fixation with fresh solutions, avoiding high concentrations of silver thiosulfates, followed by thorough washing with water free of oxidants, and drying in air free of noxious gases, are practices to be recommended for minimizing silver retention by the photographic material. Film meeting the archival requirements for residual thiosulfate and thionates is believed to possess a satisfactory low concentration of residual silver as well. Photographic prints processed to have low residual thiosulfate and thionates would also be presumed to have low silver retention.

The first test for residual silver in a photographic material appears to be the use of ammonium sulfide by J. J. Cooper[107] in 1839. Sodium sulfide is used today for this purpose, and a modern version is the following test solution[99]:

Kodak Residual Silver Test Solution ST-1

Water	100 ml
Sodium sulfide	2 g

For use, dilute one part of the above solution with nine parts of water. Diluted solution should be replaced after one week; the concentrated solution stored in a small stoppered bottle should be replaced after three months.

A drop of the diluted solution is placed on the emulsion surface in the margin of a squeegeed film or print, or on an unexposed piece of the same photographic material that has been processed in the normal manner. After 2 or 3 min, remove excess surface liquid with a clean white blotter. Any coloration more than a just-visible cream tint indicates the presence of objectionable residual silver in the film or print.

It is presumed that upon storage the margin and highlights of the photographic material would tend to reach the level of color formed by the sodium sulfide drop on the surface. Any stain more than the minimum should not be

tolerated, unless the photographic film or print is for short-time use. The sulfide stain will be formed immediately if the photographic print is to be toned in a sulfide toning bath.

Using the ST-1 sodium sulfide solution without dilution, an expedient suggested by R. W. Henn and J. I. Crabtree,[108] may produce a pink stain with certain glossy photographic papers. The baryta layer of these papers reacts with the alkaline sodium sulfide solution to form a coloration having sufficient intensity to invalidate the test results. These same investigators[109] have suggested the use of a 0.2% selenium reagent, or the dilution of a commercial selenium toner (such as Kodak rapid selenium toner) at dilutions of 1:9 or greater. Selenium is a poisonous element and should be handled with care.

American National Standard PH4.33-1969, "American National Standard method for the determination of silver in photographic films, papers, fixing baths, or residues," may be applied to the determination of residual silver in photographic films or prints.[110] The method involves a digestion of the test material and a subsequent titration with a standardized potassium iodide solution, using a pH meter. A trained chemical technician is required to carry out the silver analysis. Much more rapid methods, such as X-ray fluorescence, require elaborate equipment. For on-the-spot, qualitative evaluation of the efficiency of washing, the sulfide spot test is generally used, even though the results are qualitative in nature.

DRYING

Drying is the process of removing the water taken up by the photographic material during processing until the remaining moisture in the film or paper is in equilibrium with the water content of the surrounding air. The amount of water retained after processing depends upon the type of the film or paper and upon the processing treatment. Water retention is less in hardened, low-gelatin, thin emulsion layers and water-resistant bases. Any processing condition that causes the gelatin of the emulsion layer to swell excessively will increase the amount of retained water that must be removed during drying. At 25°C the maximum hygroscopic moisture content of gelatin is 50%, but when wetted, the maximum water content is of the order of 1500% The water retained by the gelatin may range from 5 to 20 g/sq ft depending on the nature of the photographic material.[111] (See Figure 7.)

Drying involves two stages: (1) removal of surface water and (2) removal of the water that must diffuse from within the film or paper. Approximately 50% of the total water present after washing can be removed from the surface by mechanical or chemical methods.[112] In the small-scale darkroom, where

time is not a prime factor, the surface water may be removed by swabbing both surfaces of a film with absorbent cotton, a chamois, or a photographic sponge. All contact with the film surface may be avoided if the film is bathed briefly in a water solution of a wetting agent which causes the surface water to drain uniformly from the hanging film without forming drops of water on the surfaces. The film is allowed to hang in a dust-free area until sufficiently dry to store. Photographic prints are usually freed of surface moisture by blotting or squeegeeing, then dried on cloth-covered racks, between blotters, or on ferrotyping surfaces that are often heated.

The need to remove surface water from film or prints on continuous processing machines has led to the introduction of a number of ingenious devices, commonly called squeegees, even though some do not touch the surface of the photographic material.[113] The early squeegee was a rubber blade that wiped the surface free of water but, unfortunately, had low wear resistance, eventually allowing water to escape past the blade. A more recent version is molded of solid polyurethane of good abrasion resistance and capable of removing 95% of the surface moisture on photographic film.[114] Soft-rubber wringer rollers have also been used to remove the surface water.[115]

Mechanical squeegees and rollers involve contact with the emulsion surface, which may be easily damaged. Air knives[116] and Venturi squeegees[117] use compressed air to blow away moisture from both surfaces. Blasting with air avoids surface contact, but the air must be freed of dirt and oil. The vacuum squeegee avoids the risk of dirt contamination by sucking up the water, but its use is rather noisy. Two of the more recent squeegees devised for the rapid removal of surface water include (1) the wringer-sling squeegee having one flangeless roller that wrings liquid from the surface of the film and displaces it to the large flanges of the other roller which, in turn, slings it away by centrifugal force[118] and (2) the rotary buffer[119] having two plush-covered rollers (with one on each side of the film) rotating at high speed counter to the direction of the film movement.

Surface water must be removed uniformly from the surface, or spotting and uneven markings may result. Markings which are just barely visible on film dried slowly in air at room temperatures will often become objectionable when film is dried rapidly at high temperatures.[120] Water containing a high salt content may leave a surface deposit of those salts. During drying, drops or streaks of water on the base side of a film will cool the film as they evaporate, retarding the drying of the emulsion side to produce a visible marking.[121] A drop of water on the emulsion side can produce a spot with a narrow outline that is darker than the surrounding image density, or the entire drop area may have increased density. Some spots have halos of less density than the surrounding density. Halos involving density changes are

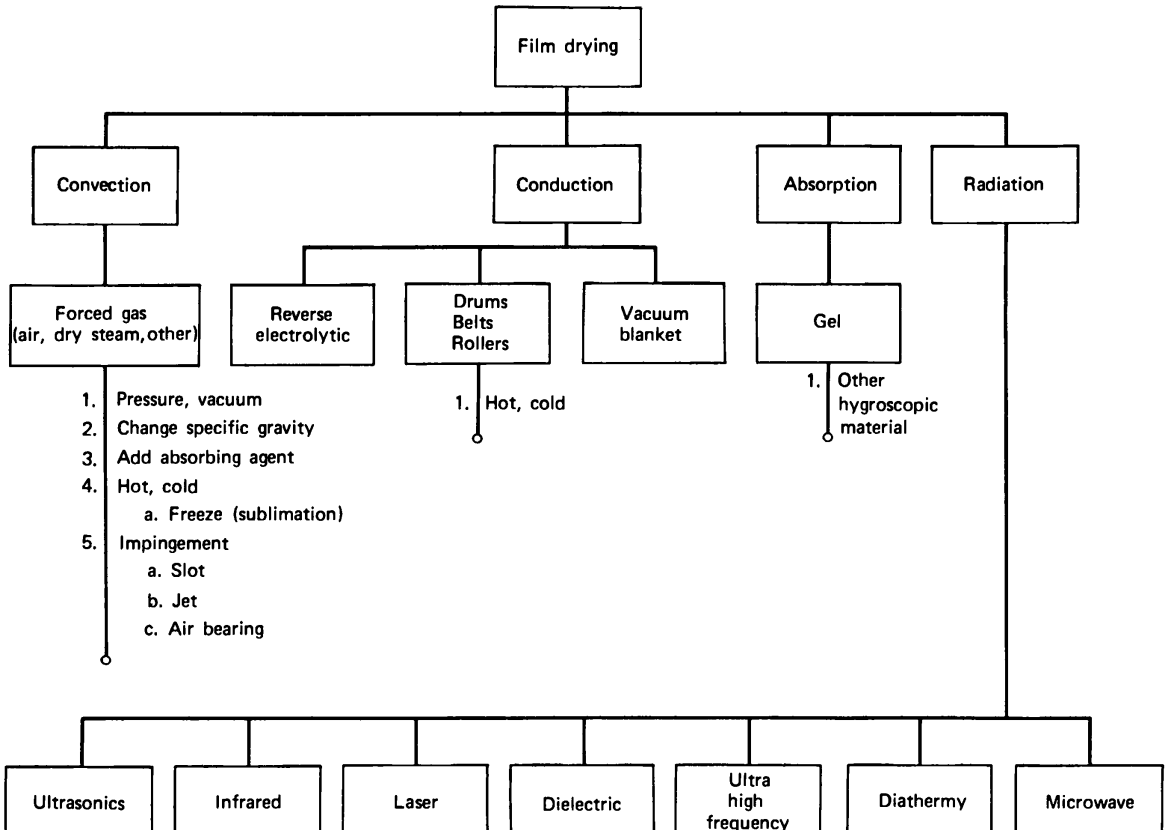

Figure 7. Convection, conduction, absorption, and radiation are the four methods of drying photographic film. [Ivan G. Ryman and William K. Overturf, *J. SMPTE*, 78: 4 (1969).]

often the result of the rate of drying of the gelatin, which affects the structure of the developed silver image.

Rapid Evaporative Drying

After the removal of the surface water, the remaining water must be evaporated until the level is low enough so that the photographic material may be stored. During the early stages of evaporative drying the rate of drying depends on the flow of drying air, as sufficient water has always diffused to the surface of the photographic material. During the last stages the rate of water diffusion falls off and the drying rate drops continuously.[122] The problem of drying film has been succinctly summarized by J. I. Crabtree[121]: "Motion picture positive film which has been fixed and washed at a temperature of 65°F and the excess moisture removed contains one pound of water per 1000 feet of film, while negative film contains two and one-half times this amount. The problem of drying is to evaporate this moisture from the film efficiently without distorting the film, and without producing drying marks, or dust spots."

The time required to dry a photographic film in air depends upon three factors:

1. *The amount of water absorbed.* The quantity of water absorbed by a film is proportional to the thickness or degree of swelling of the emulsion layer, as the film base takes up very little water (unlike the paper base of prints, which absorbs considerable water).
2. *The rate of change of air at the surfaces of the photographic material.* Air should be continuously supplied to evaporate water, rather than allowing a stagnant layer of air to become saturated with water vapor.
3. *The water content of the air used for drying.* The rate of drying is inversely proportional to the degree of the water saturation of the air; that is, air already saturated with water has no drying action, but dehydrated air has great drying efficiency.

At any given temperature the amount of water vapor in the air compared with the maximum amount needed to saturate it is called the relative humidity. Relative humidity is expressed in percent of the maximum amount of water that could be held at that temperature. For example, if air at 70°F contains one-half the water that it could contain at that temperature, then the relative humidity is 50%. A relative humidity of 100% means that the air holds all the water vapor it can at that temperature.

If air with a relative humidity of 50% at 70°F is raised to 100°F, the absolute amount of water vapor in the air is the same at both temperatures. At

100°F, however, the air is capable of holding more water vapor than at 70°F, so the relative humidity will be less than 50%. Heating air is a common method to increase its drying capacity for removing water from photographic films, plates, and papers. Air that has a low relative humidity, as in arid regions, does not need to be heated, as a fan is sufficient to insure rapid drying. In most other regions, heating the air is of definite benefit in speeding the drying action, as a lower relative humidity promotes more efficient drying.

When air is cooled by refrigeration, the relative humidity rises, eventually reaching saturation (100% relative humidity). Cooling the air below this temperature will result in the condensation of water from the air. If this cooled air is now heated, the air will have a lower relative humidity than before refrigeration, because some of the water vapor has been removed from it. Thus heating, or refrigeration and then heating, can increase the suitability of air for removing retained water from the photographic material. The lower the relative humidity (water content at a given temperature) of the air, the more rapid can be the evaporation of water from the film or prints.

The evaporation of water requires energy or heat—539 calories of heat are required to vaporize 1 g of water. Evaporation of water without the addition of heat energy will cool the photographic material, just as the evaporation of perspiration from human skin in hot climates cools the human body.

As a result of the great increase in volume—about 1600%—when liquid water is changed to water vapor during evaporation, the air near the surfaces of film or prints becomes saturated (high relative humidity). Air with high relative humidity has low drying capacity and must be replaced with air of low relative humidity if drying is to be rapid. Intensive agitation to sweep away saturated air, according to C. E. Ives,[123] can accelerate drying by a factor of 100 times as compared with conventional drying. Drying with high-velocity air, however, results in the rapid cooling of the photographic material, so a large amount of heat must be supplied at the same time.

The heat necessary to overcome cooling during drying must not cause the air to have too high a temperature or the wet gelatin layer may be seriously damaged. Heat may be supplied by conduction (heated rollers, platens, drums, and from other surfaces in contact with the film or paper base), or by radiation, such as with infrared lamps. It is usually more practical to supply the heat by convection in the drying air, often with recirculation of reheated air that still is capable of holding additional water vapor. Raising the temperature of the drying air serves both to lower the relative humidity of the air and to provide the heat necessary to evaporate the water from the surface of the film or prints.

For best results, photographic materials should be in equilibrium with air of 40 to 60% relative humidity. Sometimes film is intentionally overdried, then a suitable moisture content is restored before it is wound into a roll.

Overdrying photographic materials is to be avoided, as they will curl. If the gelatin on photographic paper "loses its original moisture content of approximately 14%, it has lost its capacity to again take up moisture. If the original 14% remains in the gelatin, excessive curl and brittleness may be corrected by simply rewashing and drying the finished print."[124] The rate of drying during the drying period should not change, or wavy markings, similar to shorelines, may mark the edges between zones of different drying rates.

Photographic film or paper dried to too low a water content is brittle, has excessive curl, and shrinks in dimension; at too high a water content, the emulsion layer is soft and sticky and is elongated in dimension.[125] The use of too high an air temperature may form a dry surface skin on the top of the emulsion layer while the inner emulsion layer remains soft and moist. This unstable condition will eventually correct itself, but if the freshly dried film is used, as in projection, the emulsion may be damaged. This case-hardening of the surface is the condition that is present in "green film" that has uneven water distribution throughout the gelatin of the emulsion layer.[113]

Rapid drying systems using air may be classified as

1. *Heat drying.* Raising the temperature of the air reduces its relative humidity and increases the drying rate of the moving air.
2. *Turbulent air drying.* High-speed dryers often use turbulent, heated air for rapid drying.[126] Air temperatures as high as 210°F and air velocities as high as 6000 fpm were utilized by F. Dana Miller.[127]
3. *Infrared drying.* Drying by radiant energy was described by Don M. McCutcheon[128] in 1939, and infrared generators were studied by Irving Ryman and William K. Overturf.[129] Unequal absorption of radiation by the darker image areas may cause wrinkling or shriveling of the film around areas of high density even when used with high-velocity air.
4. *Refrigeration drying.* A commercial dehydrator using refrigeration has been described that takes incoming air at 75°F and 60% relative humidity and produces outgoing air at 105°F and 19% relative humidity.[130] Although horsepower requirements are high, dehydration drying equipment is used for X-ray and color film processing.[112]
5. *Other drying systems.* High-frequency radio waves (microwaves just beyond the infrared region), diathermic and dielectric heating, ultrasonic squeegeeing air impingement, and vacuum techniques have also been evaluated for possible drying of photographic products.[129]

The conditions of drying have long been suspected of increasing image graininess,[131–134] but the observed increase in graininess may be more the

result of incipient reticulation formed during processing.[135] More recent tests with turbulent high-velocity air-drying of film processed in solutions at 120°F have not indicated any increase in grain size over conventionally processed film in solutions at 68°F.[136]

The conditions of temperature and relative humidity during film drying do appreciably affect the final density and contrast of the image. High humidity and high temperature gave greater density than lower values of humidity and temperature. The presence or absence of hardener in the fixing bath did not have an effect on the final densities. The increase in density or contrast is not related to the rate of drying but, according to D. R. White,[137] "Higher densities result when drying takes place under such conditions as to soften the gelatin during the process. On this view, the cooling due to evaporation becomes an important factor. When the humidity is low, the cooling is great enough to keep the gelatin firm even at the higher air temperatures; but when the humidity increases, the cooling is not as great and a corresponding softening of the gelatin takes place. This permits a rearrangement of the somewhat plate-like grains, and results in higher density from the same amount of silver."

Variations in temperature of air at low relative humidities have little effect on the photographic image, but with air at high relative humidity, density and contrast increase with increasing temperature. Drying conditions, then, should be kept reasonably uniform in order to achieve uniformity of results at different times of processing. Lower temperatures and humidities during drying would minimize the effect of variations of temperature and humidity, so it would be advantageous to use these more stable conditions for drying whenever possible.

Chemical Drying

Most film or paper is dried by evaporation of most of the retained water, often with moving, heated air. Chemical methods may be used to displace water from the emulsion layer and to shrink the swollen layer to about the thickness of the air-dried layer. The most common chemical methods of drying include the use of (1) salt solutions, (2) alcohol solutions, and (3) polymeric drying treatments.

Drying with Salt Solutions

Immersion of the washed photographic material for 1 to 2 min in a strong solution (essentially saturated) of certain salts will shrink the gelatin of an emulsion layer to almost the thickness of the dried layer. The gelatin is flexible and not sticky. Potassium carbonate was suggested[138] as a suitable

salt for temporary drying, but the photographic film should be rewashed as soon as possible. Strong thiosulfate solution (65% anhydrous sodium thiosulfate) has also been proposed as a temporary means to remove water from the film.[139] Potassium carbonate or magnesium sulfate has been suggested,[140] but the magnesium sulfate was preferred because 80 to 90% alcohol could remove all traces of it. This use of alcohol was not verified by G. W. W. Stevens,[141] who found that it promoted the rapid crystallization of the magnesium sulfate.

Stevens did find that "All these salt solutions caused swollen emulsion layers to shrink down rapidly and satisfactorily. The solutions are, however, viscous and 'greasy' and very reluctant to wet absorbent materials such as cloth, cotton wool or blotting paper. Thus, although emulsion surfaces treated with these solutions rapidly become almost as tough as fully dried layers, even repeated wiping with fresh swabs of cotton wool leaves a film of solution which eventually crystallizes. Crystallization appeared to be slowest with potassium carbonate, which is thus probably the least objectionable."

Drying with Organic Solutions

The use of methyl, ethyl, or denatured alcohol has been suggested many times for rapid drying of film, plates, or papers. Strong alcohol solutions may produce opalescence or milkiness in the emulsion layer, but pure methyl alcohol did not produce milkiness. According to J. I. Crabtree,[142] the degree of opalescence increased as drying was more rapid or the drying temperature was higher. The addition of 1% salicylic acid to denatured alcohol was found to be effective in preventing the opalescence. Strong alcohol solutions may damage some film bases by causing them to swell, and plasticizers may be extracted. Upon drying, the base may be very brittle and may cockle or curl badly.

The following recommendations were made by Stevens[141] for the rapid drying of film, plates, or prints with alcohol:

1. The drying of plates may be speeded by bathing (after washing) for 2 to 5 min in a bath containing not more than 70% ethyl alcohol by volume.
2. A 2-min treatment in 70% ethyl alcohol may be used with films, but some film base materials may be harmed.[143] Undiluted ethyl alcohol may be used with either films or plates if drying temperatures do not exceed 70°F.
3. Prints on very thin base paper may be dried rapidly by immersing for 1 to 2 min in denatured alcohol, blotting off the surface liquid, and drying in the normal way.

4. Prints on single-weight or heavier paper bases have been dried by soaking for 20 min in undiluted denatured alcohol, then pinning the print to a stick and setting fire to the alcohol running off the print at the bottom. The stick must be waved to prevent the edges of the print from becoming charred. Soaking a single-weight print for 2 to 3 min will produce almost complete drying after the alcohol has burned off, but double-weight prints cannot be dried completely. Prints on very lightweight papers have a tendency to char or burn.[144]

Alcohol evaporates more easily than water and requires less heat. It can pass into either dry or wet gelatin until the proportions of the alcohol in the solution inside and outside are essentially equal. Water in a swollen emulsion layer is partly replaced by a proportion of alcohol nearly equal to that in the solution, reducing the swelling of the gelatin layer and aiding in more rapid drying.

A solvent mixture of 25% diacetone alcohol in petroleum ether has been suggested[145] for displacing water from washed photographic materials. After a 1-min treatment with gentle agitation, the film may be removed and wiped with a soft cloth, being essentially dry. Diacetone alcohol combines with water at the surface of the emulsion layer, forming droplets of diacetone alcohol–water mixture that is insoluble in petroleum ether. When dislodged by the agitation, the droplets fall to the bottom of the container to form a heavier layer. The lower layer may be removed and the diacetone alcohol regenerated.

Polymeric Drying Treatments

Nonevaporative drying of swollen gelatin layers of photographic materials can be achieved by bringing the layer in contact with certain polymeric materials.[146,147] An example of such a substance is polyethylene glycol of the general formula

$$HOC_2H_4(OC_2H_4)_nOH$$

having an average molecular weight of from 900 to 20,000. Commercial products of this type, such as Carbowax 1540 (average molecular weight of 1540) or Carbowax 6000, are available (Union Carbide & Chemicals Corp.). (See Table 6.)

Several seconds' immersion of a washed film in a 50% water solution of Carbowax 1540 is followed by squeegeeing to remove the polymeric compound. Alternatively, the film may be immersed for 30 sec in a solution of one part Carbowax 1540 and two parts water. The gelatin emulsion layer is

Table 6. Polyethylene Glycols (Carbowax)

Commercial Name	Average Molecular Weight	Physical State
Carbowax 200	200	Liquid
Carbowax 300	300	Liquid
Carbowax 400	400	Liquid
Carbowax 600	600	Liquid
Carbowax 1000	1,000	Semisolid
Carbowax 1500 (Mixture of 300 and 1500)	500 to 600	Semisolid
Carbowax 1540	1,540	Semisolid
Carbowax 4000	4,000	Flakes
Carbowax 6000	6,000	Flakes
Carbowax 20M	20,000	Flakes

dry, but a thin layer of water–Carbowax 1540 clings to the surface. A significant increase in film density is obtained as compared with air drying, provided excess surface water is present. The difficulty of removing the residual surface layer of the Carbowax 1540 has limited the practical application of this and related compounds for polymeric drying purposes. Osmotic drying with Carbowax 1540 is more efficient than air impingement drying if the wax is recovered by evaporating the water taken up. Dryers using Carbowax are much simpler and smaller than air impingement dryers, thus less expensive.

Contact Heat Drying

Paper prints may be dried by pressing the emulsion layer side or the paper base side in contact with a polished surface. If the gelatin of the emulsion surface of a print is pressed into intimate contact with the smooth, glazed surface, the print will have a high gloss when dry, increasing the tonal range of the image by a greater richness of the black tones. Although production of a glossy surface does not depend on it, the glazing surface used for drying is usually heated to shorten the time needed to dry the print. If the paper base of a print is contacted with the heated, polished surface, the print will be

dried without glazing its emulsion side. Color prints, black-and-white matte-surfaced prints, and thin-base document and industrial papers are often dried with their paper base in contact with the heated surface.

The drying of matte-surfaced prints usually poses few problems. Light striking such a rough-surfaced print is scattered in all directions. Some of the scattered light reaches the eye, so that the photographic image becomes less contrasty and the blacks have less visual density. Fine image details are not apparent in the darker shadow areas. This image degradation can be minimized by having a glossy print surface. Almost all the light is reflected in one direction from the glossy print surface and little scattered light reaches the eye. The black areas of glossy prints are not degraded by the diffusely reflected light, and these areas are darker in tone to the eye. The range of densities has been increased as well as the visual contrast, yielding a print that reveals fine detail in the shadow areas.

Ferrotyping is the name given to the process of producing a glossy print surface by pressing the damp emulsion surface against a polished surface during drying. Positive photographic images, called ferrotypes, were formed in the ferrotype process of photography after processing an emulsion that was coated on the black-lacquered surface of iron sheets. The same black-lacquered sheets, without the emulsion layer, were used to glaze prints during the earlier days of photography. This use of ferrotyping sheets gave the name ferrotyping to the procedure of forming a glossy print surface during the drying.

The gloss of the glazed print depends upon the perfection of the polished surface used during drying. Any surface defect will be reproduced in the gloss of the print. Many surfaces may be used besides ferrotype sheets, tins, or plates made of lacquered or enameled iron. Good-quality plate glass has often been used, but it must be thoroughly cleaned with soap and water or the prints will stick to it. Cellulose acetate sheeting (film base without any coated layers) may also be used, although the surface is easily scratched. The surface need not be cleaned, but sometimes a very thin layer of Vaseline is applied to prevent print sticking. Metal sheets made of polished copper or stainless steel have also been used satisfactorily. In what is probably the most common modern ferrotyping procedure, prints are held in contact with internally heated chromium-plated convex metal sheets or chromium-plated rotating metal drums by a stretched cloth that must be kept free from contamination by inadequately washed prints.

Ferrotyping surfaces must be thoroughly cleaned when new and occasionally during use. Chromium-plated surfaces may be cleaned by rubbing gently with a soap-and-water solution. Soap and hot water, or a dilute ammonia solution, may be used to clean glass or black-enameled sheets. Waxing the enamel or glass surfaces is said to be better.[148] Commercial

ferrotype polishes are available or a ferrotype plate polish, Kodak formula P-1, may be used. This formulation is made by dissolving 0.7 g paraffin completely in 32 ml carbon tetrachloride (avoid breathing the harmful vapors of carbon tetrachloride). A tuft of cotton is moistened in this solution and then rubbed over the entire ferrotyping surface. A soft flannel cloth is used to polish the surface until no traces of the polishing solution are visible. Glass and enameled surfaces must be washed and rewaxed periodically when the previous waxing wears off. Chromium-plated surfaces are generally used without waxing.

Photographic paper having a suitable gelatin top layer is used for making prints with a glossy surface. The gelatin of the emulsion layer and the top gelatin layer must be adequately hardened, or the print will stick tenaciously to the ferrotyping surface. Prints that have excessively hardened gelatin layers, because of overhardening during manufacture or during natural aging of the photographic paper, will not glaze to a uniform gloss. Too soft a gelatin layer will deform during glazing, or the layer will adhere to the cloth during matte-drying of the prints.

Securing a uniform, high gloss during drying requires careful attention to many details of a ferrotyping procedure. More difficulties are encountered with the manual processing of photographic paper than with continuous machine processing. A definite procedure for the successful drying of ferrotyped prints is described in the American Standard Practice for Photographic Processing Manipulation of Paper, Z38.8.6-1949[149] (but not in ASA PH4.29-1962,[150] which replaced Z38.8.6-1949) and in Kodak Pamphlet G-10, "Ferrotyping Glossy Prints."

These procedures include the following suggestions:

1. After washing, the prints are put in clean water or in a glossing solution, which may consist of 5% glycerin (to help minimize print curl when the prints are dry) and a few drops of a wetting agent such as used for film drying. The wetting agent helps to secure uniform wetting of both the ferrotyping surface and the print surface, producing a more uniform gloss.

2. In applying prints to a ferrotyping plate it is essential to have a layer of water under the print and not to have any air bells trapped between the print surface and the ferrotyping surface. The following method has been suggested as the most dependable:[148] "Rinse and swab the tin thoroughly with the finger tips; wipe the print with the hand while the print is still in the water to remove any air bells clinging to the emulsion; pick up the print by two adjacent corners, transfer it over the tin, and lower it, face down, so that one edge is in contact with the tin; then lower it further in order to 'roll' the print onto the ferrotyping surface. After a short draining period, the prints should be squeegeed into contact."

Table 7. Faults in Glazing and Heat Drying

Fault	Possible Causes	Cure
Small imperfections and pittings in glass	1. Grit in washing water	1. (a) Fit water filter (b) Change filter bag
	2. Grit or dust on glazing surface	2. (a) Clean rotary glazer as it revolves (b) Load glazing plate under water after washing
	3. Rotary glazer has become electrostatically charged and is attracting dust	3. Switch off and allow to discharge
Many microscopic imperfections in glaze, no pitting, tendency to localization	1. Glazer too hot	1. Cooler glazer
	2. Exhausted fixing bath	2. Fresh fixing bath
	3. Omission of stop bath	3. Use of stop bath
	4. Omission of acid hardening fixing bath	4. Use of acid hardening fixing bath, check with litmus paper
	5. Plates or films fixed in same bath	5. (a) Don't (b) Add boric acid to make a 1% solution
	6. Electrochemical reaction between glazing surface and washing water	6. No cure
Oyster shell ring marks on glazed prints	1. Glazing drum revolving fast	1. Adjust rheostat
	2. Overhardened acid hardening fixing bath	2. Fresh fixing bath, less hardener
Wavy edges of finished prints	1. Glazer too hot*	1. Adjust rheostat
	2. Insufficient pressure on print during glazing*	2. Adjust pressure of cloth
Poor overall glaze, inconsistent in quality, no flecks or pitting	1. Poor quality paper	1. Change make of paper
	2. Print retained too long on glazer when dry	2. Remove when glazing complete
	3. Grease on glazer	3. Wash glazer with soft soap, polish with good silver polish, wash with 4% acetic acid
Prints stick	1. Insufficient hardening in fixing bath	1. Add hardener
	2. Dirty glazer	2. As item 3 above

Table 7. ***(continued)***

Fault	Possible Causes	Cure
Brown stain on finished print	*Overall*	
	1. Forcing development*	1. Don't
	2. Omission of stop bath*	2. Use stop bath
	3. Exhausted fixing bath*	3. Fresh fixing bath
	4. Washing too long in chemically impure water*	4. No cure
	Local	
	1. Insufficiently deep developer*	1. Deeper developer
	2. Prints touching in fixing bath*	2. Individual attention for first 15 to 20 sec in fixing bath
	3. Prints rise to surface of fixing bath*	3. Fix prints face downward
	4. Dirty cloth on glazer	4. Change cloth
Brownish-purple stain on finished print	1. Exhausted fixing bath*	1. Fresh fixing bath
	2. As items 2 and 3 above*	2. As items 2 and 3 above
Prints other than glossy, when heat-dried, may show defects marked * above, and in addition		
Wavy edges to finished print	1. Insufficiently dried at too low a temperature	1. Adjust speed and/or rheostat of rotary dryer accordingly
	2. Dried too quickly at too high a temperature	2. Adjust time of drying with flat bed dryer to 10 to 15 minutes
Fluff from cloth adhering to finished print	1. Dryer too hot	1. Adjust rheostat
	2. Pressure of cloth too great	2. Adjust pressure
Pattern of cloth on finished print	Pressure of cloth too great	Adjust cloth, check for shrinkage, check rotary dryer squeegee released
Loss of gloss, general dullness or may be localized	1. Dryer too hot	1. Adjust rheostat
	2. Exhausted fixing bath	2. Fresh fixing bath
	3. Plates and/or films fixed in same bath	3. (a) Don't (b) Add boric acid to 1%
	4. Insufficient hardening	4. Adequate hardening

3. Hand rollers, wiper blades, or a washing machine wringer may be used to press the print surface into intimate contact with the ferrotyping surface. All pockets of trapped air must be removed during the squeegeeing. The backs of the prints may be protected from soiling if the prints are first covered with a cloth or blotter before being rolled in contact with the ferrotyping surface. This technique will also remove excess surface water from the ferrotyping plate.
4. The prints may then be dried by allowing air to come into contact with the backs. Drying may be speeded by flowing a gentle stream of moderately heated air over the prints. Rapid heating, especially immediately after applying the prints to the ferrotyping plate, should be avoided, as an irregular gloss will result. When dry, the prints will pull away from the ferrotyping surface. They may be lifted from the surface by hand but only after they are almost dry.

Ferrotyping defects may occur both in the manual and machine methods of glazing. The use of gloss solutions containing a wetting agent and humectant tends to help achieve defect-free print glosses, especially under low humidity conditions. Such a solution tends to minimize unglazed spots due to entrapped air bells, to prevent the oyster-shell markings that result from too-rapid drying, and to keep the edges of the print from lifting before the gloss has formed. A listing of some of the faults that occur during glazing or heat drying of prints, as well as possible cures, has been compiled by James L. A. Evatt[151] and is reproduced on pages 692 and 693 (Table 7).

Heat-drying by hot ferrotyping methods may cause a shift in image coloration toward warmer tones. Many organic sulfur compounds are known to inhibit this color shift. Jozef Frans Willems and Antoon Leon Vandenberghe[152] in U. S. Patent 3,438,777 (1969) proposed the use of 5,5-*bis*-1,2,4-triazoline-3-thiones in the emulsion layer or in the photographic solutions. The compound may be included in the developing solution, the fixing bath, or in a bath just before ferrotyping or hot drying. From 0.050 to 3.0 g/liter of solution was the stated range of use of the compounds. When used in silver diffusion transfer solutions, the 5,5-*bis*-1,2,4-triazoline-3-thiones acted to prevent silver sludging in the solution.

As a final soak bath for photographic prints, Jean R. Ake[153] patented (U. S. Patent 3,404,004) a thiosulfate-removing, print-flattening composition. For 1 gal of concentrate, the following compounds were added:

Ammonium lauryl sulfate	0.85 oz.
Propylene glycol	0.05 oz.
Antifoam B (Dow Corning Corp.)	0.10 oz.
Sodium hexametaphosphate (Calgon—Calgon Corp.)	3.0 oz.
Water to make	1.0 gal

Four ounces of this concentrate was added to a gallon of water for use. A 2-min soak in this bath was followed by a 5-min wash in water.

STORAGE OF PROCESSED PHOTOGRAPHIC MATERIALS

After thorough processing, photographic films, plates, and papers are remarkably stable but are not completely resistant to the conditions of the environment. The silver-gelatin layer of a photographic material is in constant danger of degradation by various pollutants, such as harmful atmospheric gases or fungus growths. The conditions of storage of processed negatives and prints, both black-and-white and color, are extremely important in determining the permanence of the photographic record. (See Tables 8 and 9.)

The optimum relative humidity for the storage of black-and-white microfilms, sheet films, and prints is 40 to 50%; the optimum temperature range is between 60 to 80°F, preferably near 70°F.[154] High relative humidities are dangerous because of possible fungus growth on the gelatin of the emulsion layer; low relative humidities of below 15% should be avoided because under these conditions gelatin becomes brittle, and curl problems become acute. Both of these extremes must be avoided with microfilm, whose storage conditions are given in ANSI PH5.4-1970, "Practice for Storage of Processed Silver-Gelatin Microfilm."[155] For short-term storage, a relative humidity of 60% or less is specified with a temperature of 90°F or less. For archival keeping of microfilm, a relative humidity of 40% or less at a temperature of 70°F or less are recommended.

The longest life for photographic images would be best insured by near-freezing temperatures and a relative humidity of 10 to 20%.[156] The cost of constructing and maintaining such storage conditions is prohibitive, however. Processed photographic materials stored at such low temperatures and relative humidities would have to be warmed and reconditioned before use to avoid moisture condensation and brittleness. Film brittleness and curl are produced at low humidities, but flexibility of the film is regained after humidification. A lower limit of 15% relative humidity for cellulose ester base films and 25% for polyester base films has been recommended to avoid the brittleness and adhesion problems.[157]

To minimize problems resulting from storage conditions and to reduce the cost of storage, processed photographic materials (black-and-white) may be stored at relative humidities just below 50% and at a temperature just below 70°F in order to secure the best compromise of suitable conditions. Nitrate film negatives are most satisfactorily kept at 50°F and 40 to 50% relative humidity[158] but should be printed on a more permanent film base. For color materials, relative humidities from 25 to 40% at a temperature of less

Table 8. Summary of Precautions for Preservation of Photographic Film Records[154]

Required Life	Commercial Records (required life: 10 to 15 yr)	Archival Records[a] (required life: indefinitely long)
Film requirements:		
Raw film stock	Safety film of reputable manufacture	Must meet Bureau of Standards and American Standards Association requirements
Residual hypo	Fine-grain images: not above 0.01 mg/sq in. Medium-grain images: not above 0.02 mg/sq in.	Not above 0.005 mg/sq in. Not above 0.01 mg/sq in.
Residual silver salts		Film must give negative test
Storage atmosphere:		
Relative humidity	Relative humidities over 60% must be avoided; sustained low relative humidity (under 25%) is undesirable	40 to 50%
Temperature	Avoid high temperature	60 to 80°F
Air purification	Only normal cleanliness	Remove dust and acidic gases such as sulfur dioxide, hydrogen sulfide, etc.
Air conditioner	Frequent or sustained high humidities can be harmful; otherwise air conditioning is unnecessary	Essential
Protect from:		
Fire and water	Store film in cardboard cartons in metal cabinet having necessary fire resistance and located with respect to hazard from fire and water as recommended by National Fire Protection Association. If fire-resistive safe is used, film must be enclosed in vapor-tight cans to protect from steam.	Store microfilm in individual cans with loose-fitted lids inside metal cabinets in a fire-resistive vault built as recommended by National Fire Protection Association.
Physical damage	Care is required in both storage and handling. Where records are in frequent use, duplicates should be available for loan and the originals retained in storage.	
Mold	Attack by mold can cause complete destruction of records. Avoid high relative humidities as indicated above.	

[a] The conditions prescribed for archival or permanent film records are desirable for all film records and may well be adopted in any case where it is economically feasible.

Table 9. Temperature and Humidity Recommendations for Storage of Motion Picture Films[159]

16 mm Motion Picture Films	Long-Term Storage		Films in Active Use	
	Temperature (°F)	Relative Humidity (%)	Temperature (°F)	Relative Humidity (%)
Black-and-white	Below 80	40 to 50[a]	Below 80	25 to 60
Color films	50 or lower	25 to 40[a]		

[a] If relative humidity exceeds 60% for any length of time, dehumidification is required; if relative humidity is below 25% and brittleness is encountered, humidification is required.

than 50°F are recommended storage conditions.[159] Actually, lower humidity conditions (15 to 30% relative humidity) favor the preservation of the dye image.[160]

High humidity, especially at temperatures above 80°F, during storage will cause a breaking up of the filamentary structure of the silver image, apparently due to a recrystallization phenomenon of the metallic silver.[161] Storage at very high (near 100%) or very low (less than 8%) relative humidities results in a gain in image density. At the high humidities the silver image is changed by a thickening or breaking up of the filaments; at the extremely low humidities the gelatin loses water, compacting the silver filaments closer together to give a higher diffuse density.[162] The contraction of gelatin during drying has been found to exert a considerable mechanical pressure to compress developed silver filaments.[163]

PROTECTION OF SILVER IMAGE

Protection Against Attack by Atmospheric Gases

Control of relative humidity and temperature is essential for the preservation of photographic images, but the silver of the image may still be attacked during storage by gaseous pollutants in the air, such as the oxides of nitrogen and sulfur, or other sulfiding compounds. The burning of natural gas in unvented stoves and heaters may produce such noxious by-products of combustion.[164] Various peroxides, such as those often formed during the drying of fresh paint, are harmful to silver image stability. The silver image

may be made less susceptible to degradation if given a protective gold coating. One solution recommended for this treatment is the Kodak gold protective solution GP-1.[165]

Kodak Gold Protective Solution GP-1

Water	750.0 ml
Gold chloride (1% stock solution)*	10.0 ml
Sodium thiocyanate	10.0 g
Water to make	1.0 liter

* A 1% stock solution of gold chloride may be prepared by dissolving 1 g in 100 ml of water.

Add the gold chloride stock soluion to the volume of water indicated. Dissolve the sodium thiocyanate **separately** in 125 ml water. Then add the thiocyanate solution slowly to the gold chloride solution, stirring rapidly.

For use: Immerse the well-washed print (which preferably has received a hypo-elimination treatment) in the gold protective solution for 10 min at 68°F (20°C) or until a just-perceptible change in image tone (very slight bluish-black) takes place. Then wash for 10 min in running water and dry as usual.

Approximate exhaustion life: Eight 8 × 10-in. prints per liter. For best results, the Kodak GP-1 solution should be mixed immediately before use.

After washing, the photographic silver image of a print may be treated in a bath before drying in order to make the metallic silver more resistant to the attack of atmospheric gases. E. Scudder Mackey[166] patented an antifading bath that utilized the reaction product of formaldehyde with suitable ureas. Three minutes' immersion in 4% *N,N'*-dimethylolurea or 5% *N*-methylolmethylenebismonoethylurea, followed by drying, was said to prevent the fading and change in color of the silver image due to exposure to a harmful atmosphere containing the combustion products of an unvented burner using natural gas. Antifading baths containing the addition product of formaldehyde with a triazine or a hydantoin were suggested in a patent by Harold C. Harsh.[167] A 2-min treatment in an aqueous solution containing 5% trimethylolmelamine (sold under the trade name of Tanak MRX by American Cyanamid Co.) produced a print that "showed no fading or change of color in the silver images whereas the untreated print showed considerable fading and change of color." Similar formaldehyde-hydantoin reaction products were placed in an overcoat layer of a color photographic material to inhibit fungus growth, as described in U. S. Patent 2,762,708.

Prevention of Fungus Attack on Photographic Materials

Air contains many spores that can produce fungus growths on the gelatin of photographic materials. Below 60% relative humidity these spores cannot germinate. At higher humidities, especially with elevated temperatures, such as in tropical areas or under summertime conditions, colonies of fungi attack the gelatin of a black-and-white photographic image, causing filamentary veining, etching, staining, and eventual total degradation of the image. Color transparencies, negatives, and prints show similar effects as well as a change in color density near the fungus filaments because the fungus releases acids during its growth.

Fungus growth on negatives may be limited or prevented by placing the negative in a paper envelope treated with a fungicide. A suitable preservative for treating the envelope is the sodium salt of pentachlorophenol, available as Dowicide G from the Dow Chemical Company or as Santobrite from Monsanto Chemical Co. A photographically inert paper is bathed in a 2% aqueous solution or the compound may be added during paper manufacture so that 0.5 to 1% sodium pentachlorophenate is present in the paper.[168]

An effective method for the prevention of fungus growth on processed photographic images is a fungicidal rinse applied after the final water wash or even after the films or prints have dried. A 0.1% pentachlorophenol sodium salt rinse bath has been found particularly effective for prevention of fungus growth on black-and-white film and color transparencies and prints.[169] No harmful effect was noted on black-and-white or color images. Another fungicidal rinse bath is the Ansco 955 stabilizing rinse, used for stabilizing and protecting color image dyes.

Ansco 955 Stabilizing Rinse

Water (90°F)	750.0 ml
Solidogen LT 13*	30.0 ml
Zinc acetate ($2H_2O$)	10.0 g
Igepal CO 630†	0.5 ml
Water to make	1.0 liter

* Solidogen LT 13, a product of the GAF Corporation, is a cationic, quaternary ammonium compound used to stabilize dyes.
† Igepal CO 630, another GAF product, is a nonionic wetting agent of the nonylphenoxypoly(ethyleneoxy)ethanol type.

pH should be maintained at 6.2 with 10% ammonium hydroxide or 10% acetic acid.

A 3- to 5-min treatment in the Ansco 955 stabilizing rinse is followed by a 3- to 5-min water wash, then by treatment in a wetting agent solution before drying. The zinc salt of the stabilizing bath is the active fungicidal agent.

Certain ammonium compounds have proved effective in fungicidal rinses, but they may soften the gelatin of the emulsion layer. A rinse bath containing 0.5 to 1.0% zinc fluosilicate and a wetting agent has been found to be effective with black-and-white and color films.[170] Zinc fluosilicate was said to cause a yellow stain on paper prints. It has been reported that di-isobutylphenoxy-ethoxyethyl-dimethyl benzyl ammonium chloride (Hyamine 1622, Rohm and Haas Company) is "satisfactory for black-and-white prints but it should not be used for color prints and transparencies. Instead color prints should be protected by a lacquer coating containing Hyamine 3709, which is pentachlorophenol phenoxy acetate."[171] It should be mentioned that most fungicides are extremely poisonous and should be used with great caution.

Mercurial organic compounds have been patented (Japanese Patent 43-27329) for the prevention of fungal growth in photographic film emulsion layers. Suitable compounds consist of an aryl group, with or without substitution, and a diarylalkane disulfonic acid bonded to a mercury atom.

On the basis of current knowledge, the following chemical treatment is recommended to prevent fungus attack upon black-and-white photographic materials when the humidity cannot be controlled:

1. *Treating black-and white film negatives.*[172] The washed negatives should be bathed in a 1% zinc fluosilicate solution containing one part of a wetting agent, such as Kodak Photo-Flo 200 solution, for every 200 parts of the zinc fluosilicate solution. Remove any residual liquid with a damp sponge but dry without wiping unless necessary. Wash the sponge, the hands, and everything else that has been in contact with the zinc fluosilicate, as this compound is extremely poisonous.
2. *Treating black-and-white paper prints.*[173] Immerse the washed prints for 3 to 5 min at room temperatures not below 70°F, agitating occasionally in a 1% aqueous solution of Hyamine 1622 before drying. Hyamine treatment may produce a slight yellowing. This treatment is not recommended for color prints. Fungus growths on color prints and films may be retarded by lacquering the surfaces.

Aging Blemishes on Processed Microfilm

Processed negative microfilm is often used for archival storage of valuable records. It came somewhat as a shock in 1963 when stored rolls of processed

negative microfilm were reported to possess blemishes and spots in the background, the image, and on the leader.[174] These microscopic spots have been found in negative microfilms stored in rolls two to 20 years of age. Image detail may be impaired by the spots, but the image is still legible.

These aging blemishes often occur as circular microspots, ranging in diameter from 10 to 170 μ, occurring with a structure of concentric rings. The microspots have commonly been called "red spots" because of their frequent red color, but brown, yellow, and even colorless spots have been found. The silver content is lower in the central spot area than in the surround.[175] Sometimes surface mirrors are also present. Because of their wide variety of size, shape, and color, aging blemishes have been classified into six types.[176,177] Type 1 blemishes, for example, are the circular spots, usually 50 to 150 μ in diameter with a sharp boundary, consisting commonly of concentric light and dark rings that may be brown, yellow, orange, or red. (See Figure 8.)

Processed microfilms are often stored in paper cartons, although metal cans are preferred. These paper cartons were shown to emit oxidizing and reducing agents, probably peroxides, that attack the silver of the image, causing yellow or red microspots.[178] Resins of the formaldehyde-urea and formaldehyde-melamine type are used as wet-strengthening agents in these paper cartons. At high relative humidity formaldehyde, ammonia, and peroxides are released from the paper. Formic acid may result from the oxidation of the formaldehyde by the peroxide and aerial oxygen in the presence of the silver image. C. I. Pope[179] concluded that "According to the present theory, peroxide reacts with the silver in the image, forming colloidal silver which imparts a yellowish or reddish color to the blemishes." Pope did find that the wetted paper storage cartons generated peroxide when heated in an oven at 100 or 175°C.[180]

The presence of iodide ion, as from potassium or silver iodide, during development or fixation of the microfilm, gave relative freedom from microspot formation during storage of the film.[181] Some iodide may be introduced into the processing system from the silver iodide of the microfilm itself. The iodide ion may be added to the developer (0.01 to 0.10 g of potassium iodide per liter of developer) or to the fixing bath (0.2 g of potassium iodide per liter of fixing bath).

The presence of iodide ion during processing affects the nature of the surface of the filaments of the silver image. Usually some of the surface image silver reacts with the adsorbed thiosulfate to form silver sulfide.

$$2Ag^0 + S_2O_3^{2-} \longrightarrow Ag_2S + SO_3^{2-}$$

As indicated earlier, about 5 to 7% of the image silver is converted to a layer of silver sulfide on the metallic silver filaments. The presence of the iodide ion

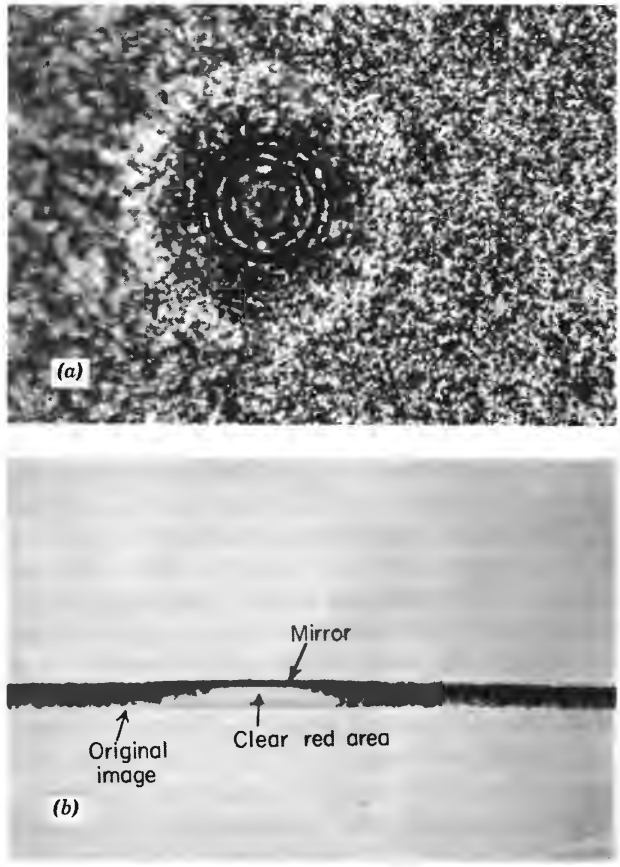

Figure 8. Microspots. (*a*) Photomicrograph at 290 ×. (*b*) Cross section at the same magnification. [R. W. Henn and D. G. Wiest, *Phot. Sci. and Eng.*, 7: 254 (1963)]

during processing inhibits this conversion of image silver to silver sulfide. With 0.2 g potassium iodide in each liter of a sodium thiosulfate fixing bath, substantially all of the sulfide is replaced in the usual levels of background densities of microfilms.[181] The surface of the silver filaments contained a layer of silver iodide, which is more resistant to oxidants that might attack the silver image. It was concluded by T. H. James[161] that the iodide retarded the recrystallization of the silver filaments by forming immobile silver complexes.

The presence of 0.2 g potassium iodide in each liter of fixing bath, supplemented with good storage conditions of the processed film, was nearly

100% effective in preventing microspot formation during four years of storage of processed microfilms.[182] This film was stored under 75°F and under 40% relative humidity but not below 15% relative humidity. The film was stored away from peroxide-containing plastics and fresh paints. Metal cans, rather than paper storage cartons, were preferred.

Sometimes storage conditions less desirable than these are unavoidable. For these conditions, microfilm images should be given a gold protective treatment.[183] The gold displaces the surface silver of the image, atom for atom. When a monolayer of gold is formed on the surface of a silver filament, it protects the filament from injurious attack that would degrade a silver image alone. The gold treatment does not increase image graininess or change the very fine structure of the image silver. A gold content of 10 mg/sq ft changed the usual warm tone of the image of many microfilms to a more neutral tone.[184] If the microfilm is to be given a gold protective treatment, the iodide content of the fixing bath should be low, as a high iodide level reduced the amount of protection given by the gold treatment.

Kodak gold protective solution GP-1 has been suggested for use to increase the resistance of silver microfilm images to attack by oxidative gases. The formula for this solution has been given in this chapter. Two other active formulas have been proposed for this purpose.

Formula 2 has now been designated Kodak gold protective solution GP-2 and a replenisher has been formulated.

Kodak Gold Protective Solution

	GP-2	GP-2R Replenisher
Water	750 ml	750 ml
Gold chloride (50% Au)	0.5 g	2.0 g
Tartaric acid	1.0 g	1.2 g
Thiourea	5.0 g	10.0 g
Sodium sulfate (desiccated)	15.0 g	18.0 g
Water to make	1.0 liter	1.0 liter

The replenisher is used at the rate of 1 ml/ft of 16mm film or 20 ml/sq ft of film processed. An improvement in the physical properties of the treated film and improved resistance to fungicidal attack are obtained if a formaldehyde hardener, such as Kodak special hardener SH-1, is used following the gold protective treatment.

Kodak Special Hardener SH-1

Water	500 ml
Formaldehyde (37% solution)	10.0 ml
Sodium carbonate monohydrate	6.0 g
Water to make	1.0 liter

Recommendations for the use of GP-2 and the formaldehyde hardener involve either a postprocess treatment of dry film or the in-process treatment of wet film.

	Formula 1[174]	Formula 2[183]
Gold chloride (50% Au)	0.4 g	0.5 g
Thiourea	1.0 g	5.0 g
Tartaric acid	1.0 g	1.0 g
Sodium sulfate (desiccated)	60.0 g	15.0 g
Water to make	1.0 liter	1.0 liter

Processed negative microfilm (dry) was soaked for 80 sec in running water at 80°F, immersed in the solution of Formula 1 or 2 for 100 sec at 80°F (agitation at 10-sec intervals), and then washed 160 sec in running water at 80°F.

Only aurous gold (Au^+), but not auric gold (Au^{3+}), is active in gold protective solutions. When thiourea is added to a solution of auric chloride ($HAuCl_4 \cdot 3H_2O$, approximately 50% Au^{3+}), the auric gold is reduced to the active aurous form. The gold ions are not free in solution but exist as a complex with the thiourea, which is present in excess to prevent the gold ions being reduced to metallic gold in the solution. The amount of gold formed on the silver image filaments depends upon the gold content of the solution, the time of treatment, and the degree of the agitation. Other conditions, such as solution temperature or density or silver content of the image, have relatively little effect upon the amount of gold deposited.

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Chapter 15
Sensitometry

The production of a perfect picture by means of photography is an art; the production of a technically perfect negative is a science.

FERDINAND HURTER AND VERO C. DRIFFIELD[48]

It should be realized that the negative is only a means to an end, and that it is the quality of the finished positive that matters.

J. F. DUNN[49]

With the wet collodion process the photographer learned by trial-and-error the most successful methods to coat and expose his own plates. Wet collodion plates were essentially the same in light sensitivity, regardless of who made them. The silver halide gelatin dry plates that were introduced toward the end of the nineteenth century offered convenience and greater sensitivity than the wet plate, but plate speeds varied widely among manufacturers. Some measure of the rapidity of dry plates was needed to avoid wastage of materials and the loss of photographic opportunities. Sensitometry was the name given to the estimation of the sensitivity of photographic materials; the term now also includes the systematic evaluation of the many characteristics that

influence the sensitivity, such as the processing conditions of the photographic film or paper.

When an emulsion layer is exposed and processed, the transparency of the layer is reduced by the deposition of developed silver. The blacker the layer, the less light gets through. Transparency may be defined as the ratio of the light passing through the emulsion layer and film base to the light that was originally incident upon the photographic material:

$$\text{transparency} = \frac{\text{intensity of transmitted light}}{\text{intensity of incident light}}.$$

The loss of transparency is influenced by the exposure, the type of photographic emulsion, the conditions of development, and other factors.

Exposure (E), one of the factors that influences transparency, is the result of a constant light intensity, denoted by I and often measured in meter-candles, acting for a given time, denoted by t and measured in seconds. Exposure is equal to the intensity multiplied by the time ($E = I \times t$, or $E = It$), representing the quantity of light measured in meter-candle-seconds received by each unit area of the emulsion layer. In the general discussion in this book, exposure, intensity, and time will be denoted as specified above. Attention should be called, however, to the growing use of E for intensity and H for exposure in national and international standards, where these designations may be listed here as now specified.

Exposure is the product of the time (measured in seconds) and the illumination (for many years measured in meter-candles). The current trend is to express exposure in lux-seconds, and these units are often found in modern methods of determining the speed of photographic materials. Exposure can also be expressed in ergs/cm^2, the amount of energy reaching a surface.

Exposure ($E = It$) is a fundamental relationship proposed by Robert Bunsen and Henry Roscoe, who found that a photochemical reaction is proportional to the product of the intensity of the light and the time in which the light acts. In 1899 astronomer Karl Schwarzchild noted, however, as did others, that at high or low intensity levels (very short or very long exposure times) photographic materials did not produce similar developed densities even though the exposures were equivalent. Thus, photographic exposure is often stated with the time specified so as to indicate any unusual circumstances where the Bunsen-Roscoe law may not apply.

Captain W. de W. Abney[1] in 1887 studied the loss of transparency of gelatin plates as the exposure increased. For exposing the plates he used a sensitometer, an instrument that produced a series of exposed areas of related values (exposure decreased by one-half for every third area). His results, after development of the plate, were diagramed to show the continuous loss of the

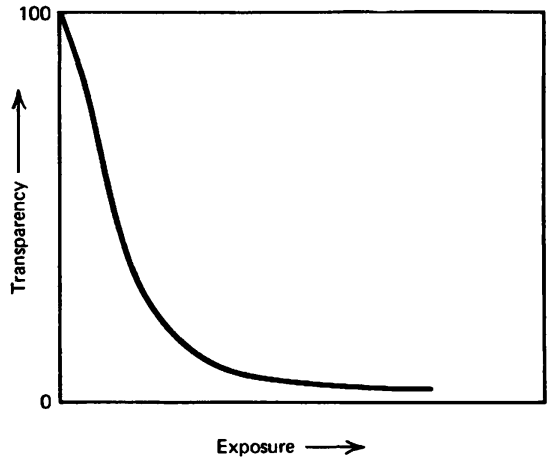


Figure 1. Loss of transparency of gelatin-silver halide plates with exposure.

plate's transparency with increasing exposure, as in Figure 1. Increasing values of transparency (actually, transmittance) rise vertically to 100% (or 1.0) for complete transmittance of all light striking the emulsion layer, and increasing values of exposure move to the right. The curve represents corresponding values of exposure and plate transparency, showing a rapid initial loss of transparency followed by decreasing losses at the higher exposure levels.

Abney's graphical results showed that at no exposure, very little or no silver was developed, and the transparency of the plate was near unity; that is, 100% of the light was transmitted. As the exposure increased, the silver deposit became progressively heavier and the plate transparency was steadily reduced. Abney tried to describe mathematically the relationship between transparency and exposure but was not successful.[2,3]

Two amateur photographers, Ferdinand Hurter, a chemist, and Vero Driffield,[4] an engineer, were also disturbed by the variability of the sensitivity of the early dry plates. They spent about 10 years of their spare time seeking a simple way by which an amateur photographer might determine the photographic speed of his dry plates. The amount of silver produced by exposure and development could be determined by removing the processed emulsion layer of a plate, then separating the silver from the gelatin and weighing the silver. This method of relating exposure to the amount of image silver was highly impractical, so a simple, nondestructive method was sought. Once a reliable method of estimating the mass of silver given by light exposure and development could be devised, then the sensitivity of the photographic material could be rated.

In 1890 Hurter and Driffield announced that "we are now in a position to trace the connection between the densities of a theoretically perfect negative and the light intensities which produced them." They had found that the light-stopping power of a silver deposit was related to the amount of silver produced by exposure and development of the emulsion layer. Previously, Abney had studied the relationship of the transparency of the plate as related to the exposure. Hurter and Driffield studied opacity; that is, the reciprocal of the transparency:

$$\text{transparency} = \frac{\text{transmitted light}}{\text{incident light}}$$

$$\text{opacity} = \frac{\text{incident light}}{\text{transmitted light}}$$

With transparency, complete passage of the incident light through the emulsion layer means that transparency is 1.0, and this value decreases to values less than 1.0 as the exposure increases. Opacity represents the light-stopping action of the silver image, having a value of 1.0 when there is 100% transmission of the light through the emulsion layer. Opacity starts with a value of 1.0 and increases in value as the silver deposit increases in blackness on the negative. The opacity is 2.0 for 50% light transmission, 10.0 for 10% light transmission, and 100.0 when only 1% of the light gets through the silver deposit of the negative. When the light transmission is 0.1%, the value of the opacity is 1000, a value that might be encountered in a dense negative.

Hurter and Driffield's major finding was that the opacity of the silver deposit was proportional to the amount of silver resulting from exposure and the kind and degree of development under suitable conditions. Exposures generally were given so that each adjacent small exposed area on the same plate received twice the exposure of the preceding area; that is, the exposures

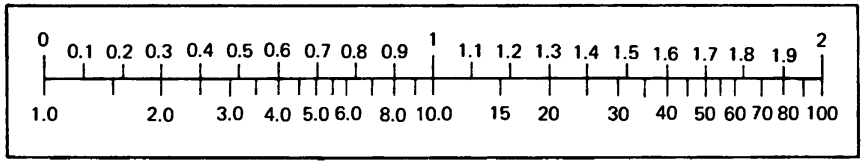


Figure 2. Relationship between linear and logarithmic numbers is shown by this scale. The top scale has equally spaced divisions (linear) whereas the spacing of the lower scale is logarithmic. The numbers in the top scale represent the logarithms of the numbers in the bottom scale. Thus, the logarithm of 40 is 1.6. [Beverly Dudley, *Photo Technique*, 2 (1): 28 (1940)]

were in the order 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, 1024, and so on. Both the opacity and the relative exposures involve large numbers (in the thousands) that are difficult to handle, so Hurter and Driffield proposed to take the logarithms of these values, as this would result in the use of small numbers. (See Figure 2.) The logarithm of the opacity they called density. Density values increased vertically on a graph, and the logarithm of the exposure increased horizontally to the right from the zero value at the intersection of the two scales. This was a convenient way to study the variation of density with increasing exposure.

Percentage Transmission	Transparency	Opacity	Log Opacity or Density
100	1.0	1	0.0
50	0.5	2	0.3
25	0.25	4	0.6
10	0.1	10	1.0
1	0.01	100	2.0
0.1	0.001	1,000	3.0
0.01	0.0001	10,000	4.0
0.001	0.00001	100,000	5.0

Logarithms were taken of the relative exposure values:

Relative exposure:	1	2	4	8	16	32	64	128	256	512	1024
Logarithm of relative exposure:	0.0	0.3	0.6	0.9	1.2	1.5	1.8	2.1	2.4	2.7	3.0

A scale length of only three units covered an exposure range of 1 to over 1000. The opacity of the negative increased as the exposure increased, and the density (logarithm of opacity) of the image was given by the values

Opacity:	1	2	4	10	100	1000
Density:	0.0	0.3	0.6	1.0	2.0	3.0

An opacity range from 100% light transmission (opacity = 1) to 0.1% light transmission (opacity = 1000) can be covered by only three units in the density scale. By plotting the density-log exposure values on a graph, Hurter and Driffield obtained a graphical representation of the relationship of these values as shown in Figure 3.

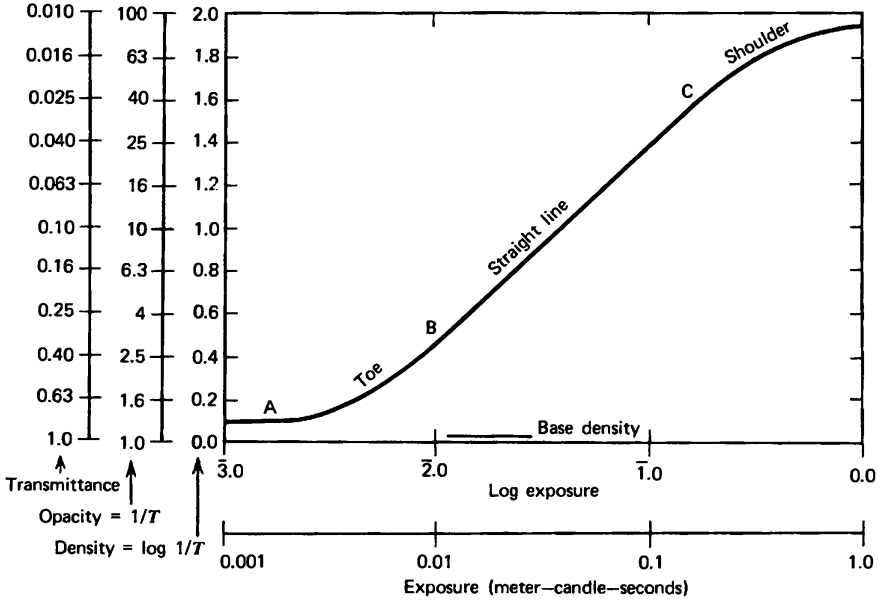


Figure 3. The characteristic curve of a photographic material. [Eastman Kodak Company]

EVALUATION OF THE CHARACTERISTIC CURVE

The characteristic curve (Figure 4) consists of a number of regions that describe the response of a photographic material:

1. *Region of no response.* In the region of extremely low or no exposure, the characteristic curve parallels the line of no density but does not coincide with it. Photographic images on film are not completely transparent in these unexposed areas but possess a slight but unvarying density. Some of this opacity may be due to the film base or the gelatin layers coated upon the base. Some density may result from development of unexposed silver halide grains (fog) or from the reduction of indiscriminately exposed silver halide (from lens flare). It is general practice to measure the fog + base density and use this value in the region of no light response. This steady, low-density value, referred to as the minimum density or *D*-min, causes the *D*–log *E* curve to begin slightly above the no-density line. In some cases the *D*-min has been subtracted from all densities, making the *D*–log *E* curve touch the line of zero density. This practice, however, fails to take into account that fog silver is not distributed uniformly over all levels of image density.[5,6]

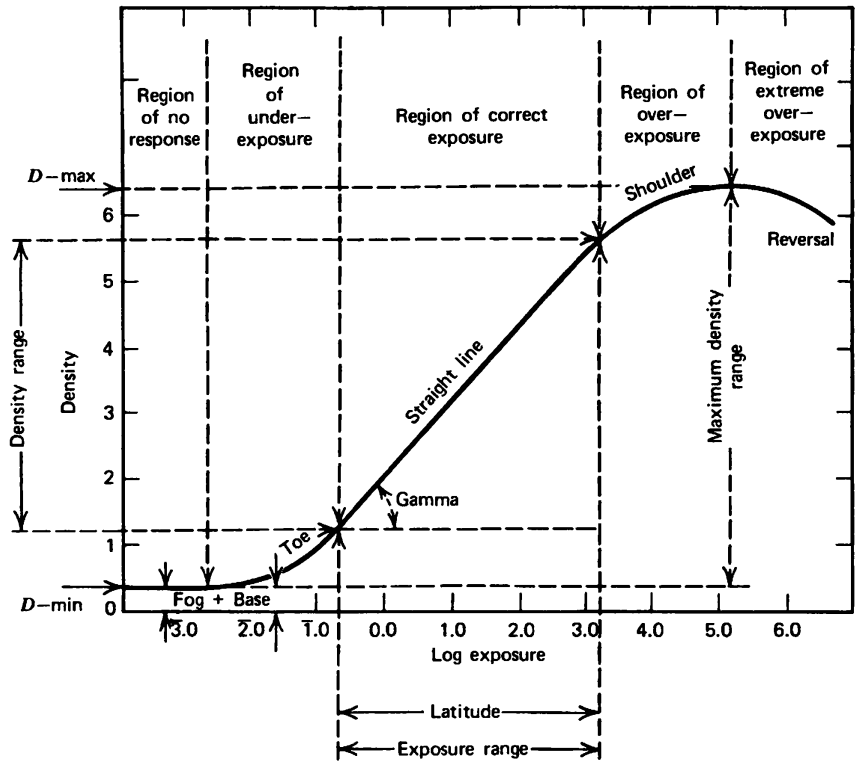


Figure 4. Regions on the characteristic curve showing response to exposure.

2. *Region of underexposure.* At first the D–log E curve follows the horizontal minimum density line, because extremely low levels of light exposure fail to form a developable latent image in the photographic material. At the point of first measurable response to exposure, the threshold point, the D–log E curve begins to curve ever so slightly upward. This is the beginning of the toe (sometimes called the foot) of the characteristic curve.[7] In this region a considerable change in exposure produces only slight changes in density, resulting in severe tone distortion of the underexposed image. There are fewer distinguishing tones recorded on the film than were present in the original subject. This tone compression produces a rendition on the film that is too low in contrast (flat), and the shadow areas lack detail.

3. *Region of technically correct exposure.* This is the region in which Hurter and Driffield sought to produce their scientifically perfect negatives. It is the straight line of the D–log E curve. Here, the blackness of the developed silver

increases proportionally with exposure. Each increment of exposure yields a given increment in density as long as the exposure falls within the straight-line region. The straight-line concepts of Hurter and Driffield apply only in the absence of light flare and for a limited object luminance. In practice with a camera, the lowest excellent exposure utilizes the toe area of the curve as well as the straight-line portion.

4. *Region of overexposure.* This region of decreasing slope, the shoulder of the curve, is not used in normal practice. Exposures greater than those of the straight-line region are recorded here as high densities. Increasing exposures produce smaller and smaller increases in density, compressing or distorting the tone scale of the subject. The areas of the subject reflecting the most light would be affected the most, so the highlights would lack tone differentiation. Negatives having such high densities would have increased graininess and would require long exposure times in printing. The maximum density of the negative occurs when the shoulder of the curve reaches its maximum height.

5. *Region of extreme overexposure.* Density decreases when exposure increases in this region of vast overexposure. The result is called solarization or reversal.[8] Sometimes this region is deliberately used for pictorial effect. The chemical constitution of many modern photographic emulsions inhibits solarization, even with vast overexposure. With practical exposures, however, this region of overexposure is not reached, and the D–log E curve does not show a reversal effect.

The graphical method of interpreting the photographic process can be used to show important relationships between exposure, development, and the resulting image density.

Latitude

The effect of increasing exposure is to move the exposure range of the subject along the length of the characteristic curve as shown in Figure 5. The latitude is the exposure range for which the density is proportional to the exposure. Projecting the length of the straight-line portion of the curve on the line of zero density determines the exposure range of a technically perfect negative. This exposure range is the latitude for that particular film exposed and developed in a specified manner. As the slope of the straight line of the D–log E curve becomes steeper, as by extending developing times, the projection of the straight line encompasses a shorter range of exposure. The selection of an exposure value to utilize the straight line of the D–log E curve becomes much more critical with inherently high-contrast photographic materials or with any photographic material developed to a high contrast.

When exposing subjects having a low brightness range, the latitude of a high-speed film may be several times the exposure range of the subject. Several values of exposure would still record on the straight-line portion of the curve. In this case, the lowest value of the exposure that records the subject on the straight line would be the most desirable. Greater exposure, although still being recorded on the straight line, would only yield higher densities and possible image degradation (more scattering or diffusion of light during exposure and greater graininess of the developed image), but the tone scale rendition would not be any better than with the lower exposure. Exposure, not development, determines where the subject rendition is obtained on the negative.

Density Range

If the straight-line portion of the D–log E curve is projected onto the density axis (the line of zero exposure), the density range of this exposure region may be determined. This is the density range where exposure produces a proportional change in the blackening of the negative. The maximum density range of the negative, however, is greater than that related to the straight-line tone rendition. The maximum density range of the negative is obtained by subtracting the minimum density from the maximum density. The maximum density range includes the region of both straight line and compressed tone rendition.[9]

The density range of the image is determined by the degree of development. At a low degree of development the exposure latitude is broad but the density range is low. As development proceeds, the latitude is shortened and the density range becomes greater. When the density range reaches its maximum value, the difference between the densest black on the negative and the minimum density is a maximum. The contrast is at a maximum. Because of the limited latitude, the tone rendition of the subject may be badly distorted, resulting in a harsh rendition of only a limited number of tones.

Gamma

Gamma is the name given to the slope of the straight-line portion of the characteristic curve, often represented by the Greek letter gamma (γ). Gamma is the slope of the straight-line portion of the characteristic curve, mathematically referred to as the tangent of the angle between the straight line and the horizontal line. It is conventional to graph density and log E in units of the same length to aid in the determination of gamma and to provide a better visual estimation of the gamma to those who deal with D–log E curves. In

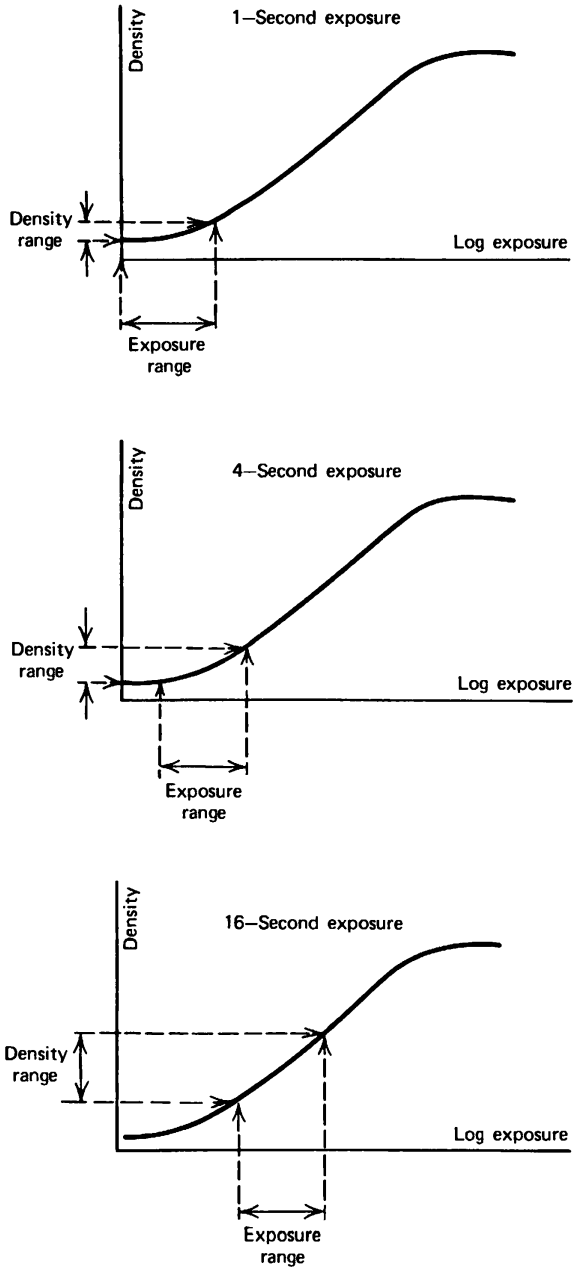
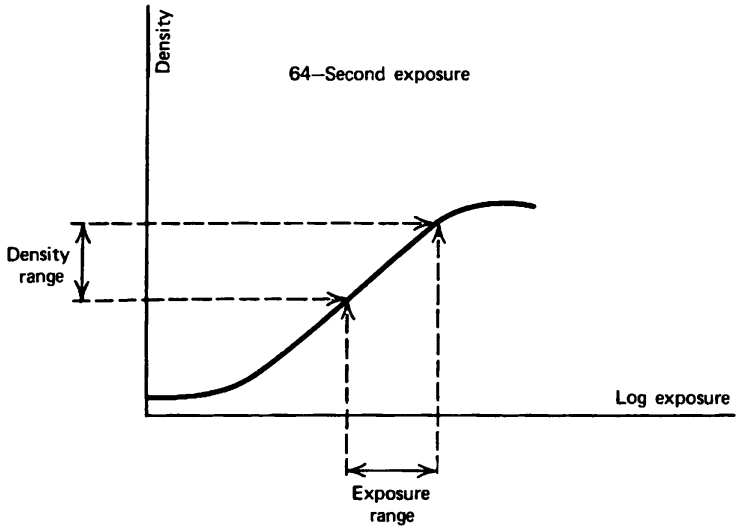


Figure 5. Effect of exposure on density range of negative.



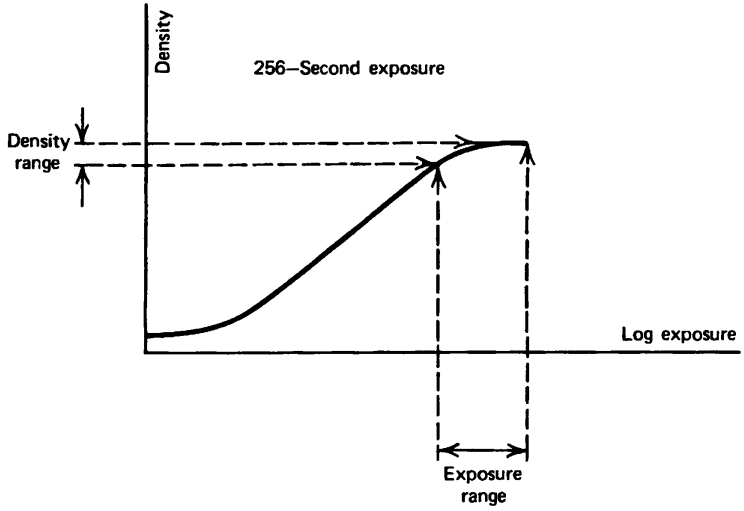


Figure 5. (*continued*)

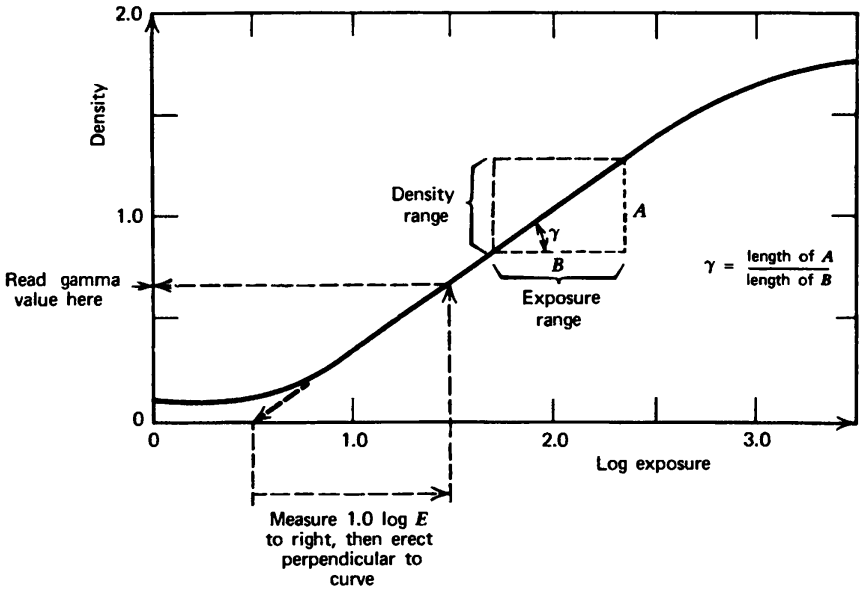


Figure 6. Determination of gamma.

this case, the straight-line portion of the curve may be extended down to the line of zero density to find the inertia point. By measuring to the right 1.0 log E, erecting a perpendicular line to intersect the D–log E curve, and from this point running a line to the left parallel with the log E axis to the density axis, it is possible to read the value there as the gamma of the characteristic curve. (See Figure 6.) Gamma may also be determined through the use of transparent gamma meters that compute the tangent value of the slope of the straight line.

Straight-line gamma is a measure of the tone rendering of the negative. At a gamma of 1, the tone rendition of the negative approximates the tonal relationships of the original subject photographed (camera flare limits exact rendition). At a gamma less than 1, the tone range of the subject has been compressed in the rendition on the negative; at a gamma more than 1, the tone range has been expanded. Development of an exposed negative to a gamma greater than 1 can compensate for a lack of contrast in the original subject, and development of a negative to a gamma less than 1 can help to reduce the contrast of a harshly lighted subject. Gamma is a measure of contrast but is not identical with it, as exposure range is also a factor in describing contrast.

Different times of development of a photographic material will produce a family of characteristic curves that will have different gammas. Gamma will be found to increase rapidly at the shorter times of development, but the increase in gamma is much less per increment of time at the longer times of development. Eventually, a maximum value of gamma, called gamma infinity (γ_∞), is reached. When the value of gamma for each time of development is plotted against the time of development, a time-gamma curve is obtained. Such a graph often shows the rapid rise in gamma at shorter times of development and an approach to the limiting value of gamma at the longer times of development. Time-gamma curves for the development of a film in a number of developers are usually available from the manufacturer of the film. It should be realized that the D–log E curves and the time gamma curves supplied by a film manufacturer may be idealized—that is, average aim curves that are not duplicated by every batch of film. For precise photographic work, therefore, D–log E curves and time-gamma curves should be prepared by the user from the film that is to be used. (See Figure 7.)

Through practical tests, the optimum gamma has been established for a large number of classes of picture-taking situations. A gamma of 0.5 to 0.7 has been found appropriate for most black-and-white amateur photography and for indoor portraiture. In the graphic arts, gamma values of 1.0, sometimes much greater, are most suitable. It is now common practice to develop film to a specified gamma that has been found most suitable for each type of photography. The development time necessary to produce the desired gamma is determined from the graph of the time-gamma relationship for the film-developer combination. It is essential that the same development conditions (temperature, agitation) be used as specified for the preparation of the time-gamma curve.

Contrast Index

Gamma is a useful measure of the degree of development, but in practice it may be somewhat difficult to measure accurately. Some modern photographic emulsions do not have a straight-line portion, but their characteristic curve bows continuously upward. It is not unusual to have a bump in the center part of the curve with straight line portions of different slope on either side. Such curve distortions may result from a blended emulsion consisting of grains of different inherent speed and contrast, or from the use of a compensating developer that may produce density at lower exposures while minimizing it at the higher exposures. Curves with extremely steep slope, such as those resulting from lith development, have such high gamma values that a

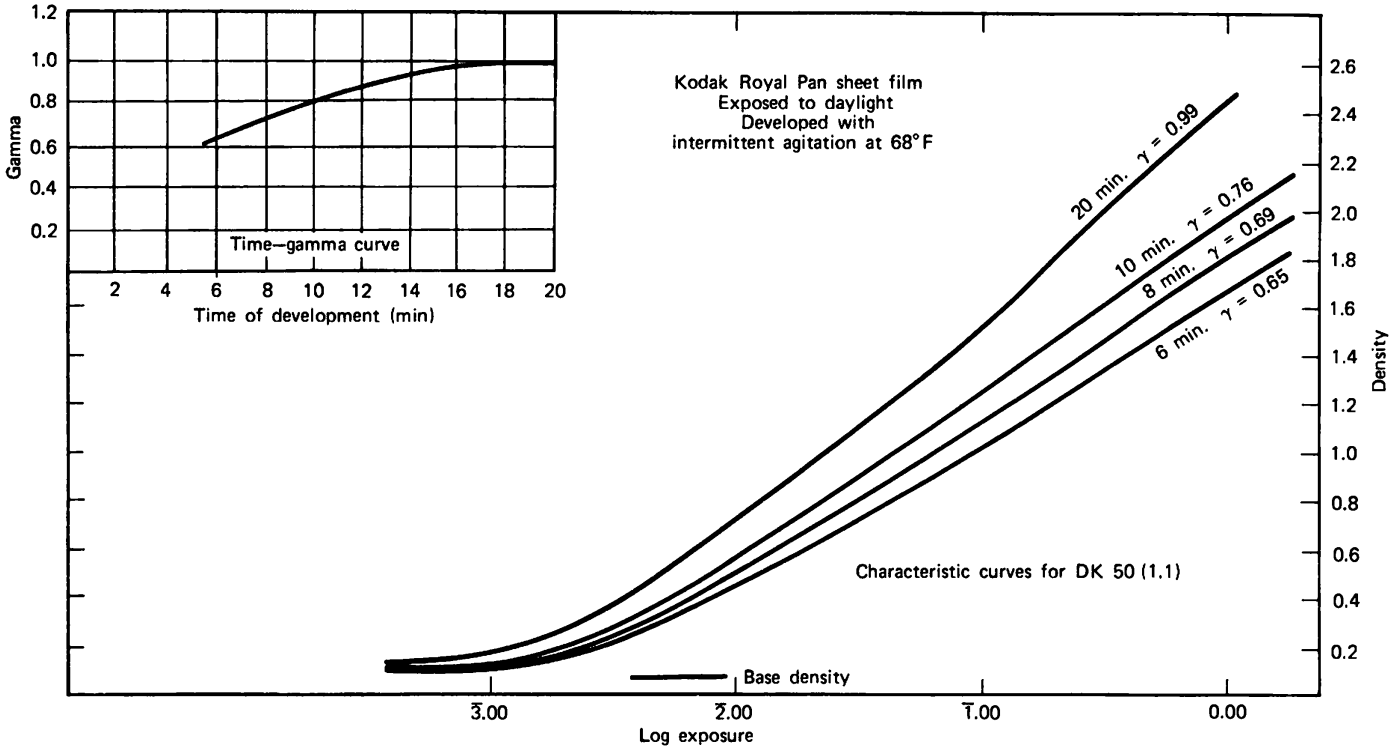


Figure 7. Characteristic and time-gamma curves for a specific film. [Eastman Kodak Company]

slight error during measurement may produce a considerable error in the value of the gamma.

Gamma, as a means of selecting development times, may be unsatisfactory with photographic materials having unusually short or long toe shapes of their characteristic curves. The best-quality photographic prints are often the result of exposures that record the image both on the toe and the straight-line portion of the film's characteristic curve. Negatives with equal density range are needed, so printing may be done on the same grade of paper. Continuous-tone negatives having different shapes for their characteristic curves may be printed on the same grade of paper if the negatives are developed to a certain average gradient rather than to a certain gamma value. The gammas of the negatives may vary considerably, but equal density ranges corresponding to equal average gradients would permit all the negatives to be printed on the same grade of photographic paper.

The inadequacies of gamma have led to attempts to specify the gradient or slope connecting two points on the characteristic curve, the points not necessarily on the straight line. Choosing the point of least exposure that is not on the straight line allows us to measure some effect of the contribution of the toe to the final tone rendition. The upper point for a gradient determination is on the straight line, because the shoulder with its high densities and poor tone separation should be avoided. The slope of the straight line connecting the two points on the curve represents a value that is less than the value of the gamma of the curve. Gradient measurements for development of different emulsions of various toe shapes and various lengths of toe have been found in practice to give more consistent photographic results than the gamma measurements.

The specification and measurement of suitable average gradients has been more difficult than the specification and measurement of gamma. An average gradient measurement for choosing the correct development times for determining continuous-tone film speeds is given in American National Standard Method for Determining Speed of Photographic Negative Materials (Monochrome, Continuous Tone), PH2.5-1960. A modification and extension of the average gradient of the Standard has been proposed and given the name of Contrast Index.[10,11] Contrast Index (CI) is being promulgated by Eastman Kodak Company and has relaced gamma in some of their publications.[12] (See Figure 8.)

Contrast Index is the average gradient of the D–log E curve between two arbitrary points on the curve representing the low and high densities. According to C. J. Niederpruem, C. N. Nelson, and J. A. C. Yule,[10]

The minimum densities lie on the arc of a circle having a radius of 0.2 in density or log exposure units. The maximum density lies on the arc of a circle having a radius 2.0

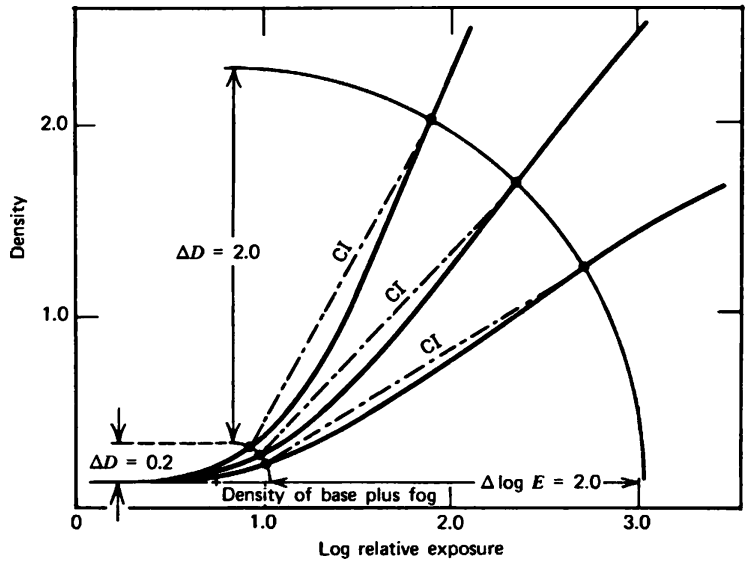


Figure 8. Contrast Index (CI) has been proposed as a replacement for gamma. The contrast index is the slope of a straight line that joins specified minimum and maximum densities on the *D*–log *E* curve of the photographic material. The minimum-density point lies on the arc of a circle having a radius of 0.2 density units. The maximum-density point lies on the arc of a concentric circle that has a radius 2.0 greater than the smaller circle. [Eastman Kodak Company]

greater than the radius of the smaller circle. The two circles are concentric and their center lies on the base-plus-fog axis. The log *E* position of the center point is that which allows an imaginary straight line, originating at the center, to pass through both the maximum and the minimum densities simultaneously.

The measurement of Contrast Index is said to be greatly simplified through the use of a transparent Contrast-Index Meter.

For most negative films for amateur, commercial, motion-picture, and portrait photography, the minimum densities lie between 0.05 and 0.15, the maximum densities between 1.0 and 1.4 above the fog-plus-base densities. Contrast Index varies with development time and may be plotted against it to produce the equivalent of a gamma-time curve. Latitude represents the useful log exposure interval from a point on the toe to a point on the shoulder. If the exposure and development are both selected to use the toe of the curve, as is the recommended practice, there will be little or no latitude for reduced exposures but considerable latitude for greater exposures.

Film Speed

An accurate and practical method of determining the speed of a photographic plate or film has been the motivating goal in expanding the science of photographic sensitometry. The need to know the sensitivity of their photographic plates caused Hurter and Driffield to begin their search for a means to rate the speed of their plates. They noted that when a number of D–log E curves representing different times of development in a low-bromide developer were drawn on one graph, then the extension of their straight-line sections intersected the zero-density line (the log exposure axis) in a point through which all the lines passed. Such a common point did not move as a result of the degree of development. This point was called the inertia point and represented a certain log exposure value.

Hurter and Driffield used this inertia point, measured in meter-candle-seconds of exposure, to help define the speed of the photographic emulsion by the relationship

$$\text{H and D speed} = \frac{34}{\text{inertia value}}$$

The 34 was arbitrarily chosen to yield a number of convenient size for use on the Hurter and Driffield Actinograph, an exposure calculator that they had devised. In addition, they noted that the steepness of the characteristic curve increased with the degree of development. The slope of the curve could be used as a measure of the degree of development, making possible a control to limit the density value obtained from a given exposure.

H and D speeds, however, are not independent of development unless the developer is free from bromide and does not produce fog. No account is taken of the shape or the length of the toe of the curve. The early Watkins and Wynne speed-rating systems were also based on inertia, suffering the same limitations. H and D numbers, and those of the related systems, were sometimes grossly abused by less scrupulous manufacturers, causing a search for a less ambiguous method for rating the sensitivity of photographic materials.

In 1894 J. Scheiner,[13] an astronomer, used the exposure to produce a density just perceptibly different from fog as a measure of photographic sensitivity. This method of threshold speed rating was also misused by some photographic manufacturers to overrate the speed of their products. In Germany, an improved threshold-measuring system was worked out to define more precisely the techniques of obtaining film speeds. Threshold measurement was made but at 0.1 density above fog. The sensitometric

wedge (30 steps, each differing by 0.1 density value), the exposure time ($\frac{1}{20}$ sec), the light source and filtration, and the developer were all stipulated. Development was continued until the maximum speed number was obtained (the number of the last step of the wedge that has a density 0.1 above fog). The results were expressed in degrees DIN (Deutsche Industrie Norm). W. B. Ferguson[14] says DIN was a contraction for "Das Ist Normal" (that is standard). The DIN system was an improvement but could have impractical rating numbers because of the shape of the toe of the curve. Extended development, although producing a maximum speed rating, produced high contrasts that were not encountered in normal development. Other speed-rating systems adopted a density much higher than those used by the Scheiner and DIN systems.

The early methods of sensitometric evaluation of photographic speeds were usually made by photographic scientists who often used controlled light sources to contact-print a stepped or continuous-wedge tablet on the photographic material. Sometimes, rotating wheels with open sectors were used to moderate the light between the source and the photographic material. Photographers, however, must use an optical projection system in their cameras to form the image for exposing their film or plates. When light passes through a lens, some of the light is scattered, and this light falls indiscriminately upon the emulsion to expose it. The effect of this flare light is appreciable in the areas of least exposure—the toe of the D–log E curve. As J. F. Dunn[15] has pointed out, "It is in practice almost impossible to work on a straight part of the negative characteristic curve anyhow owing to the effect of flare." The early concept of Hurter and Driffield's perfect negative with a straight-line tone rendition was largely a fallacy because the D–log E curve of the negative formed in the camera, not in a scientific experiment, must be used to make the print.

Satisfactory prints, not perfect negatives, are the goal of black-and-white photography. Loyd Jones and his associates[16,17] approached the problem of rating film speeds from the standpoint of the exposure necessary to produce a quality print. Photographic prints were made from negatives having different levels of exposure, then groups of observers selected the "just acceptable" and the "first excellent" prints. These prints were then related to the parts of the D–log E curves of the film materials used to make the negatives. In this way the print was used as the criterion for determining the exposure necessary for the negative to give a quality print.

The toe area of the film characteristic curve was found to be used for making a quality print. The useful lower limit of the toe region can be adequately specified, not as a certain density above fog plus base density but as a function of the average gradient of the D–log E curve.[18] The average gradient was measured as the slope of two points located on the curve, one point being in

the toe region. The present American Standard and British Standard film speeds are based on the concepts which Jones and his associates so voluminously documented.

This incomplete review of the early efforts at rating the speed of films and plates makes it evident that meaningful sensitometry of a photographic material is a complex and difficult endeavor. Keith M. Hornsby has said in his book, *Sensitometry in Practice*, "It cannot be emphasized too strongly that there is no system for determining the sensitivity (or speed) of a photographic material which is applicable to all types of material; every method so far devised is based upon an expression of sensitivity which depends on certain emulsion characteristics. If two widely different emulsions are compared using one system, it is quite possible that another system would give quite a different picture of their relative sensitivities." Yet the photographer needs a rating of the sensitivity of the photographic material in order to determine a useful exposure.

Current speed-rating systems for films are useful for different applications. For monochrome, continuous-tone film negatives of pictorial subjects, the American National Standard method described in ANSI PH2.5-1972 is applicable for determining the minimum exposure that gives a satisfactory result.[19] This method does not apply to materials that are used for high-contrast copying, aerial film exposures, photorecording, scientific (astronomical or spectrographic), or cathode-ray-tube recording. The sensitivity of color materials, reversal or negative, is rated by their own standard methods. Manufacturers of these specialized products have devised methods of expressing sensitivity different from that of ANSI PH2.5-1972. In many cases the rating method is similar, but the selection of the speed point may vary considerably from that of ANSI PH2.5-1972.

THE SPEED OF PHOTOGRAPHIC MATERIALS

Monochrome Film for Continuous-Tone Use (American National Standard Method PH2.5-1972)

Testing Conditions

Sensitometer:	Nonintermittent illuminance-scale type.
Exposure time:	Between $\frac{1}{20}$ and $\frac{1}{80}$ sec.
Light source:	Incandescent lamp at a color temperature of 2850°K.

Filtration: Double cell, containing two solutions of copper and other compounds to produce light of artificial sunlight quality.[20]

Latent image conditioning: Not to be processed before 1 hr and not later than 2 hr after exposure.

Composition of developer (pH = 9.4 ± 0.2 at 20°C):

Water, distilled (airfree), 125°F	500.0 ml
Monomethyl-para-aminophenol sulfate	0.5 g
Sodium sulfite (desiccated)	40.0 g
Hydroquinone	1.0 g
Sodium carbonate (anhydrous)	1.5 g
Sodium bicarbonate	1.0 g
Potassium bromide	0.2 g
Water, distilled (airfree), to make	1000.0 ml

Development temperature: 20 ± 0.3°C

Developer agitation: Developer is placed in specified vacuum flask and the flask is oscillated 45 deg above and below horizontal at a rate of 1 cps. At the same time, the flask is rotated about its axis once every 5 sec.

Development time: Develop several film samples from 2 to 8 min, removing them at about 1-min intervals. Select the film sample nearest to give a density of 0.80 above the density of 0.1 plus base density plus fog at a point 1.3 log E units in the direction of greater exposure from the speed point. The average gradient is 0.62.

Fixing: After development, fix twice the time to clear (vigorous agitation for the first 30 sec of immersion) but no longer than 15 min in the following solution (pH approximately 4.4 at 20°C):

Distilled water (55°C)	600 ml
Sodium thiosulfate, crystalline	240 g
Sodium sulfite, desiccated	15 g
Glacial acetic acid	20 ml
Sodium tetraborate, pentahydrate	15 g
Aluminum potassium sulfate	15 g
Distilled water to make	1000 ml

Washing and Drying: Wash in water (20 ± 5°C) for 15 to 25 min, then dry (after removing surface water) in evenly circulated air at atmospheric conditions such that the drying time is not less than 15 min.

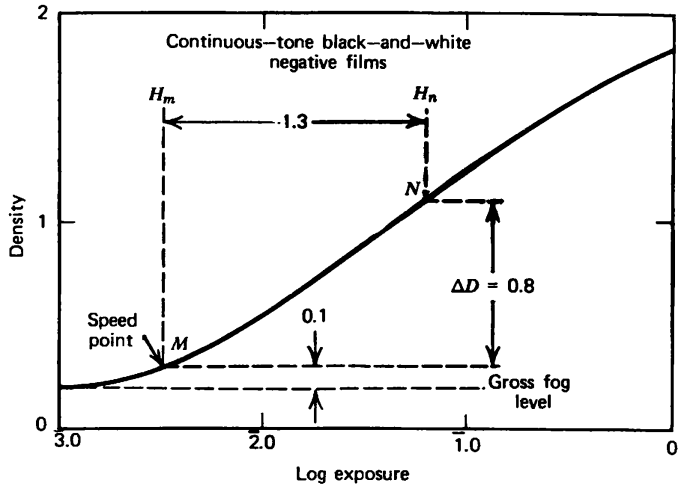


Figure 9. Density–log exposure graph for determining speed of continuous-tone monochrome film. [Graph from Derek Keeling, *Brit. J. Phot.*, 117: 676 (1970)]

Speed point: This point is located at a density of 0.1 above the fog plus base density (point *M* on the density–log exposure curve). (See Figure 9.)

Determination of speed: The American National Standard speed, *S*, is given by the formula

$$S = \frac{0.8}{H_m}$$

where H_m is the exposure (expressed in lux-sec) corresponding to point *M* on the density–log exposure curve.

Safety factor: The formula does not give the minimum useful exposure for a normal scene but rather only 0.8 that speed, thus providing a safety factor of 1.25.[21] This American National Standard speed may, for convenience, be designated as "ASA" when used with a specific value, such as ASA 64.

The use of 0.1 density above fog plus base density as one point in the determination of speed makes possible international standards for photographic speed, as this is the criterion used in the DIN system as well. A relationship, although inexact, can be used as a practical means to convert one measure of speed into another. As worked out by J. L. Simonds,[22] Table 1 relates American Standard values to DIN speed values.

Table 1. Conversion Among Various Measures of Speed

American Standard Exposure Index[a]	Logarithmic Exposure Index[b]	DIN Speed from Equation (2)[c]	DIN Speed from Equation (3)[d]
1000	41°	28.5/10°	29/10°
800	40°	27.6/10°	28/10°
650	39°	26.7/10°	27/10°
500	38°	25.7/10°	26.10°
400	37°	24.7/10°	25/10°
320	36°	23.8/10°	24/10°
250	35°	22.8/10°	23.10°
200	34°	21.9/10°	22/10°
160	33°	21.0/10°	21/10°
125	32°	20.0/10°	20/10°
100	31°	19.1/10°	19/10°
80	30°	18.2/10°	18/10°
64	29°	17.3/10°	17/10°
50	28°	16.3/10°	16/10°
40	27°	15.3/10°	15/10°
32	26°	14.4/10°	14/10°
25	25°	13.4/10°	13/10°
20	24°	12.5/10°	12/10°
16	23°	11.6/10°	11/10°
12	22°	10.4/10°	10/10°
10	21°	9.6/10°	9/10°
8	20°	8.8/10°	8/10°
6	19°	7.6/10°	7/10°
5	18°	6.9/10°	6/10°
4	17°	6.0/10°	5/10°
3	16°	4.8/10°	4/10°
2.5	15°	4.0/10°	3/10°
2.0	14°	3.1/10°	2/10°
1.6	13°	2.2/10°	1/10°
1.2	12°	1.0/10°	0/10°
1.0	11°	0.3/10°	0/10°

[a] Arithmetic exposure index.

[b] Logarithmic exposure index: LEI $= 5 - 10 \log_{10} E_{0.3\bar{G}}$

[c] Equation (2): DIN $= 0.030 + 0.939(\log_{10}$ exposure index)

[d] Equation (3): $\log_{10}$ (exposure index) $= 1.048$ DIN.

The DIN speed, as defined in the German standard, was obtained by the formula

$$\text{DIN} = \log_{10} \frac{0.36}{E_{0.1}}.$$

A DIN speed of 2.0 is written as 20/10° DIN.

Color Reversal Films for Still Photography (American National Standard Method PH2.21-1972)

Testing Conditions

Sensitometer: Nonintermittent illuminance-scale type.

Exposure time:

Film Balance	Exposure Time (sec) Roll Film	Sheet Film
Daylight	$\frac{1}{20}$ - $\frac{1}{80}$	$\frac{1}{20}$ - $\frac{1}{80}$
3200°K	$\frac{1}{5}$ - $\frac{1}{25}$	1–5
3400°K	$\frac{1}{20}$ - $\frac{1}{80}$	1–5

Light source: To conform to PH2.29-1967 or PH2.35-1969.

Latent image condition: To be processed not sooner than one day but before 10 days after exposure.

Processing: In accordance with film manufacturer's recommendations.

Method for determining film speed: Point T (Figure 10) is placed on the curve at a density of 0.20 above the minimum density.

From point T a line is drawn tangent to the curve, locating point S. If point S is located at a density greater than 2.0 above the minimum density, point S is then taken on the curve where the density is 2.0 above the minimum density.

The exposure, H_m, is computed from the exposures, H_s and H_t, corresponding to points S and T, by the relationship

$$\log H_m = \frac{\log H_s + \log H_t}{2}$$

Speed is computed from the formula

$$S = \frac{10}{H_m}$$

where

S = the American National Standard speed

H_m = the exposure (measured in lux-seconds).

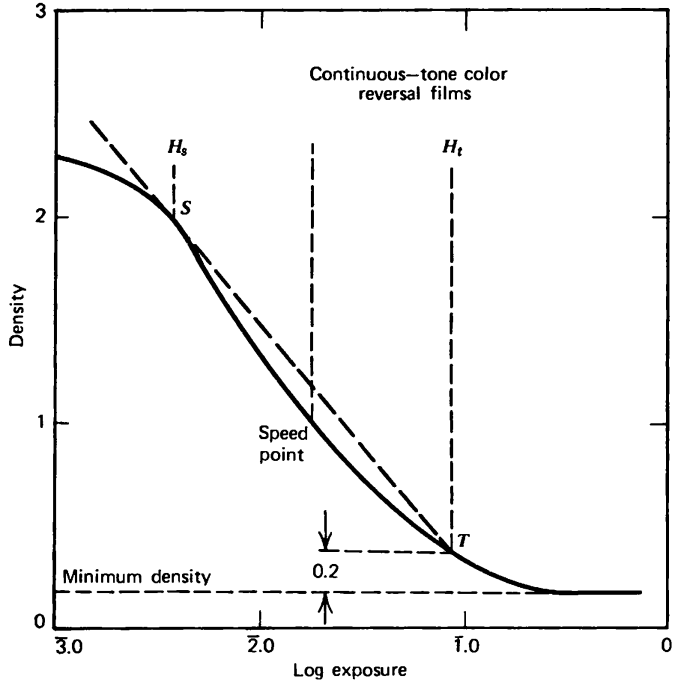


Figure 10. Density-log exposure graph for determining film speed of color reversal films. [Graph adapted from Derek Keeling.[23]]

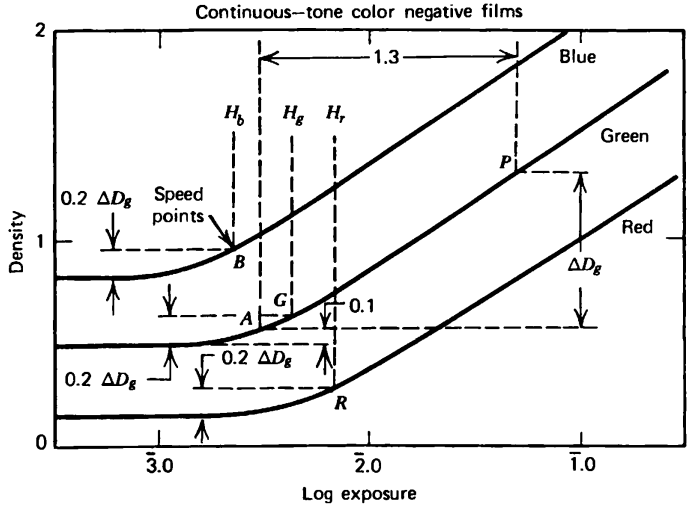


Figure 11. Density-log exposure graph for determining film speed of color negative films. [Graph adapted from Derek Keeling.[23]]

Color Negative Films for Still Photography (American Standard Method PH2.27-1965)

Testing Conditions

Exposure:	Appropriate for color balance of the film.
Exposure time:	Midpoint of range indicated by manufacturer.
Latent image condition:	To be processed not less than 5 days or more than 10 days after exposure.
Processing:	As recommended by manufacturer.
Method for determining film speed:	Point A (Figure 11): At density of 0.1 above the minimum green level (D-min). Point P: At 1.3 log exposure units from point A in the direction of greater exposure. The density difference between points A and P is designated ΔD_g. Speed points R, G, and B: At density of $\frac{1}{5}D_g$ above the minimum red, green, and blue levels with corresponding exposures H_r, H_g, and H_b meter-candle-seconds. The mean log exposure, $\log H_m$, is given by $$\log H_m = \tfrac{1}{3}(\log H_r + \log H_g + \log H_b)$$
Speed determination:	American National Standard speed, S_x, is computed from the formula $$S_x = \frac{1}{H_m}$$ where H_m is the exposure in meter-candle-seconds.

CHARACTERISTICS OF PHOTOGRAPHIC PAPERS

Photographic printing paper contains considerably less silver halide than a photographic negative film. Maximum developed density of an exposed photographic paper is low, particularly because of surface reflections. The densities of images on paper base are read by reflection, not by transmission as with photographic film. Photographic papers usually do not reach a reflection density of more than 2.0 for their developed images. The limitations of photographic paper are not really a handicap; Loyd A. Jones and C. N. Nelson[24] have reported that "the useful maximum density of the printing paper was, on the average, considerably below the available maximum

density, while the useful minimum density of the paper was usually very close to, and often equal to, zero density."

Scientific studies of acceptable print quality and the lessons of practical experience have shown that satisfactory-to-excellent prints are obtained when the effective density range of the negative is approximately equal to the log exposure range of the printing paper. This matching of the characteristics of negative and printing paper requires close control of exposure for maximum print quality. The current sensitometric standard for evaluating photographic paper is PH2.2-1966, American Standard Sensitometry of Photographic Papers, which is described below.

Sensitometric Characteristics of Black-and-White Contact or Enlarging Photographic Papers (American Standard PH2.2-1966)

Exposing and Processing

Sensitometer:	Nonintermittent intensity scale type.	
Exposure time:	Within the range of 0.1 to 10 sec.	
Light quality:	Tungsten-filament lamp operated at 3000 ± 25°K color temperature.	
Latent image conditioning:	As soon as possible after exposure, elapsed time not exceeding 2 hr at 20°C and 55% relative humidity.	
Developing solution:	Distilled water, about 50°C	500 ml
	Monomethyl-para-aminophenol sulfate	3.1 g
	Sodium sulfite (anhydrous)	45.0 g
	Hydroquinone	12.0 g
	Sodium carbonate, monohydrate	80.0 g
	Potassium bromide	1.9 g
	Distilled water to make	1000 ml
	For use, dilute one part of the above solution with two parts of water, and use at 20 ± 0.5°C. Fresh solution is required for each test.	
Development technique:	Five $1\frac{3}{8}$ × 10-in. sensitometric strips of paper are fastened to an 8 × 10-in. glass plate and then immersed in two liters of the working solution of the developer in an 11 × 14-in. tray. Agitation is provided by rocking a tray at a rate of $7\frac{1}{2}$ complete cycles per minute. Each cycle consists of one motion in each of the four directions that a tray can be rocked.	
Development time:	Ninety seconds or the development recommended by the paper manufacturer.	

Stop bath: Immediate immersion for 15 sec in the following solution at 20 ± 5°C:

Acetic acid, 28%	45 ml
Distilled water to make	1000 ml

Fixation: Samples are transferred for 5 min to the following solution at 20°C:

Distilled water (50°C)	600 ml
Sodium thiosulfate, crystalline	240 g
Sodium sulfite, anhydrous	15 g

Agitation is given for the first 30 sec of the immersion. Before use, the fixing bath should have been seasoned by fixing 160 sq in. of unprocessed photographic paper for 10 min in each liter of fixing bath.
Washing may be in running water (20 ± 5°C) for 15 min or in six changes of water with 5 min between each change of the water.
Drying shall be carried out in air at temperatures of 25 ± 10°C and a relative humidity of 55 ± 10%.

Plotting the Density–Log Exposure Curve for Photographic Paper

The values of the reflection densities are plotted on the vertical axis and the values of log exposure (measured in meter-candle-seconds), the units for both axes having equal spacing.

Locating Points on the Curve

Point *a* (Figure 12): on toe at 0.04 density above fog + base density.
Point *b*: on shoulder at 0.9 the maximum shoulder density.
Point *c*: on shoulder where gradient has diminished to 0.05.
Speed point: on curve at 0.6 density above base + fog density.
Speed formula: The American Standard Paper Speed, S, is determined by the formula

$$S = \frac{1000}{E_{0.6}}$$

where $E_{0.6}$ is the exposure in meter-candle-seconds needed to obtain a density of 0.6 above the fog + base density.
Log exposure range = $\log E_b - \log E_a$.
Density range = $D_b - D_a$.

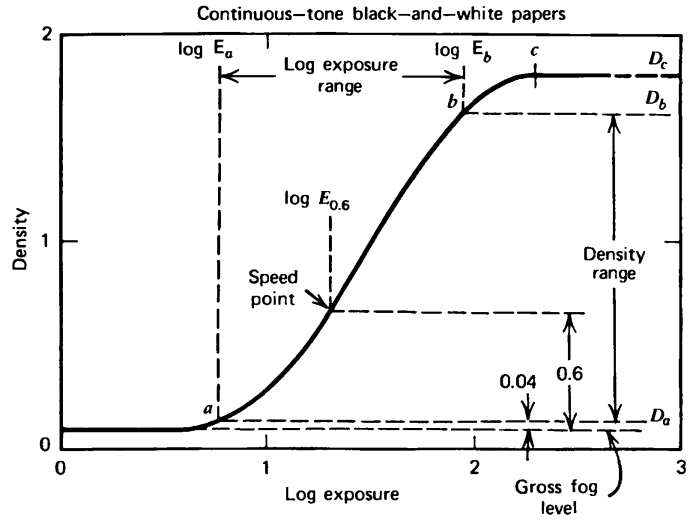


Figure 12. Desnsity-log exposure graph for determining the speed of continuous-tone black-and-white photographic papers. [Graph adapted from Derek Keeling.[23]]

Scale Index of Photographic Papers

Scale Index is an aid in selecting a grade of photographic paper that will best fit a given negative. A standard method has been described (PH2.2-1953) to determine the log exposure scale of a photographic paper—that is, the log value of the effective exposure range of the photographic paper. This value, rounded off to the nearest number following the decimal point, is the Scale Index of the paper. (See Figure 13.)

Printing Paper Grades

Satisfactory photographic prints usually result when the photographic paper has a log exposure range approximately equal to, or slightly more than, the effective density range of the negative. Photographic papers have been given numbers, called grade numbers, ranging from 0 to 6, that increase with the contrast of the paper; that is, the log exposure range of the paper decreases with increasing grade number. In addition, there is usually a word description of the contrast of the paper that corresponds to the log exposure range. A Grade 5 paper having an exposure range of 0.5 to 0.65 may be described as

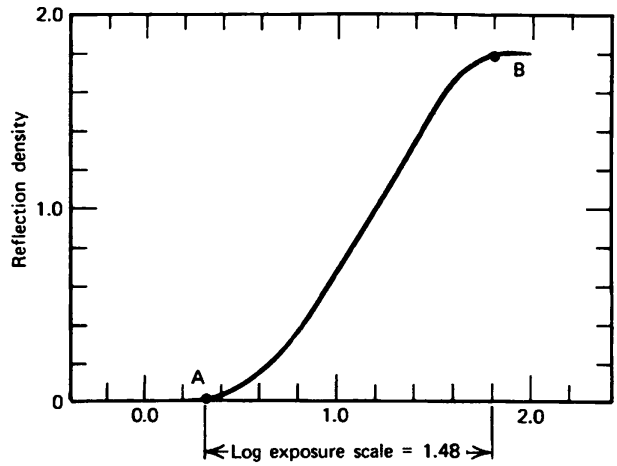


Figure 13. Method for obtaining Scale Index of a photographic paper from the log exposure scale. The Scale Index is 1.5, the value of the log exposure scale rounded to one place following the decimal. [Eastman Kodak Company]

extra hard. The relationships between the log exposure range of a paper and its classification are shown below. (See also Figure 14.)

Log Exposure Range	Description	Grade Number
0.50 to 0.65	Extra hard	5
0.65 to 0.80	Very hard	4
0.80 to 0.95	Hard	3
0.95 to 1.15	Medium	2
1.15 to 1.40	Soft	1
1.40 to 1.70	Very soft	0

Paper Contrast

The contrast of a photographic paper is not defined in PH2.2-1966 because "contrast is a complex quantity that involves log exposure range, maximum density, density-versus-log exposure curve shape, and certain characteristics of human vision." Supplementary information is provided, however, for finding a measure of the D–log E curve's slope called bar gamma, $\bar{\gamma}$. Bar gamma is found by superimposing a transparent template (with two parallel

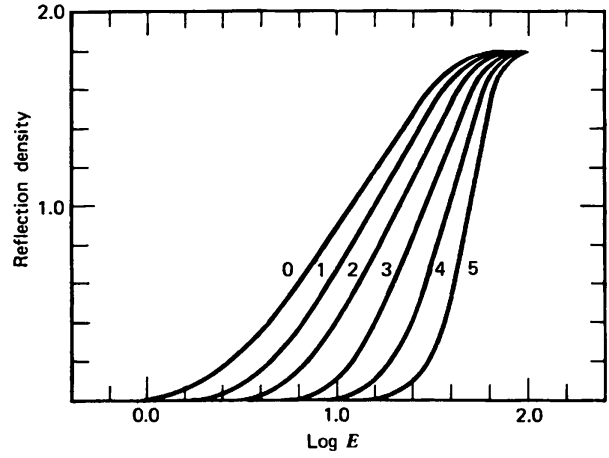


Figure 14. Characteristic curves of glossy photographic paper, grades 0 through 5. [Eastman Kodak Company]

lines 0.1 log E scale units apart) over the D–log E curve of the paper. The left line of the template is made tangential to the high-density portion of the curve and the right line to the low-density portion. Bar gamma is the value of the slope of these framing lines after alignment of the template. Bar gamma is one measure that may be employed to describe the characteristic of a D–log E curve. (See Figure 15.)

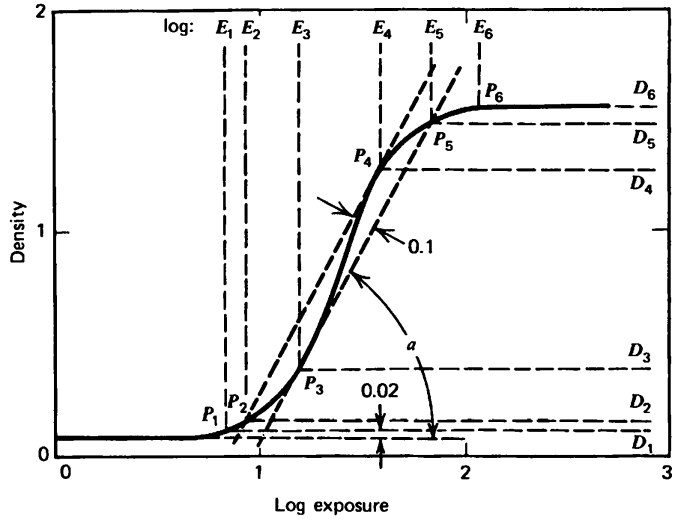


Figure 15. Graphical illustration of method of determining bar gamma as a measure of paper contrast. [Graph by Derek Keeling.[23]]

SENSITOMETRIC PROBLEMS INVOLVED IN EXPOSURE AND IMAGE EVALUATION

Sensitometry is a science made necessary by the needs of photographic practice. Photographic film speed, for example, is required for estimating film exposure, but film speed, itself, is not a fundamental, unvarying property of a photographic emulsion; it is an index obtained from a set of specified test conditions. Other indices are obtainable from other specific conditions. A sensitometric determination must involve a complete description of the exposing light, the exposure time, the processing conditions, the method of determining the image densities, the graphical or mathematical means necessary to specify the desired quantity, such as speed or the slope of the curve, and other contributing factors.

The search for the most useful values to be of aid in practical photography is hampered by our lack of understanding of the laws that govern the response of the photographic emulsion. Deviations from our present knowledge make it more difficult to characterize photographic materials than to understand simpler systems that follow known laws of response. Seemingly atypical behavior of photographic materials, either during exposure or during evaluation of the processed image, indicates the failure of our present understanding of the response of the photographic emulsion or image.

Reciprocity Failure

The general law of photochemical reaction, formulated by Bunsen and Roscoe in 1876, states that the exposure is equal to intensity (illuminance) multiplied by the time of illumination; that is, $E = I \times t$. This law was not derived for photographic materials but for photochemical reactions in general. The Bunsen-Roscoe law involves a reciprocal relationship between illuminance and time. If a given value of exposure is selected, then I and t may be any values whose product yields the selected exposure. For example, equal photochemical effects should be produced by an exposure of 100 meter-candles for 1 sec or of 1 meter-candle for 100 sec.

The photographic effect given by constant exposure is not independent of the intensity of the exposing light. Photographic exposure depends upon the rate at which energy is absorbed, and not solely upon the total amount of energy absorbed. Photographic emulsions have a response that departs from the reciprocal relationship of $E = I \times t$ when values of I are either very small or very large. This deviation from the Bunsen-Roscoe law is often called the "failure of the reciprocity law." or "reciprocity law failure," even though, more correctly, what fails is our understanding of the response of the photographic emulsion.

Reciprocity failure of an emulsion occurs during either high-illuminance, short-time or low-illuminance, long-time exposures. These exposures produce less density than at less extremes of exposure, the exact effect of reciprocity failure being dependent on the nature of the emulsion itself. The failure to follow the reciprocity law of exposure may produce, though not necessarily, a change in the shape of the characteristic curve depending on the exact conditions of exposure. The change in the shape of a D–log E curve was explained by Loyd A. Jones and V. C. Hall[25] in 1928 as "a change in the effective homogeneity of the emulsion." This concept has been totally discredited by modern emulsion makers, who control reciprocity failure during emulsion making or by aftertreatments, such as baking or treatment with hydrogen.

The reciprocity failure of a photographic emulsion is usually explained today in terms of latent image formation. During the early stages of growth, the latent image consists of a few silver atoms. Thermal energy may eject an electron from one of these silver atoms, or an electron from a silver atom may be removed by a bromine atom liberated during exposure. A bromide ion may be formed by the union of the bromine atom and the electron, thus negating the effect of the photons of the exposing light. The electron may be captured in some other way as well. The silver ion, formed by the loss of the electron, may wander away from the latent image site. Unless the latent image is built up faster than the silver ions are lost, it will be destroyed and the effect of the exposing light will be lost.

With low-intensity exposures, the efficiency of latent image formation is lowered.[26] Because of the slow release of electrons by the relatively scarce incident photons of light, the latent image can build up only very slowly. During this initial stage of formation the latent image is relatively unstable and may be dissipated by thermal disintegration or chemically induced action. This loss of latent image causes less density to be produced than at more favorable exposure conditions. The photographic emulsion is said to have suffered low-intensity reciprocity failure.

Exposures at high intensity are inefficient for another reason—the slowness of the migration of silver ions through the crystal to the latent image site. A high-intensity exposure floods the crystal with photo-released electrons. These electrons gather at latent image specks, but the silver ions cannot reach the specks in sufficient quantity to neutralize the electrons. The latent image speck becomes negatively charged, repelling other electrons, and latent image formation is limited by the slow rate of silver-ion migration. The repelled electrons may be captured by the bromine atoms formed during the exposure. A large number of the photoelectrons are thought to be captured internally in the crystal.[27] Such internal latent image sites are usually unavailable for development, wasting the effect of the exposure that released the electrons. Sites on the surface may not be built up to a developable state even

though the sublatent image is stable.[28,29] High intensity causes a loss in developed density, because the latent images are not built up to a sufficient size. In practice, a photographic material exposed at high intensity may be treated with a uniform low-intensity exposure to help overcome the reciprocity failure due to the high-intensity exposure. J. H. Webb and C. H. Evans[26] demonstrated that a high-intensity exposure could be built up with high efficiency by such a low-intensity exposure.

Reciprocity failure occurs during the initial stages of latent image formation. With low-intensity exposure there are simply not enough electrons available to form stable latent image specks or to form stable-and-developable latent images. The size of the silver halide plays a part because finely divided silver halide crystals with their limited cross-section area to intercept the exposing light would capture only a very few photons. Too few photons may be available to form stable and developable latent image specks. The larger crystals, with their greater area, would be more likely to form one or more latent images of developable size. The effect of low intensity would be relatively greater for the smaller rather than the larger crystals, as was pointed out by L. A. Jones and V. C. Hall.[25]

One method for showing reciprocity-law failure for a photographic material determines the exposure ($I \times t$) necessary to produce a constant density value at different levels of the intensity (I) of the exposing light. A graph is then constructed with log It on the vertical scale and log I on the horizontal scale. If the reciprocity law were valid for photographic materials, a horizontal straight line would result. A bowed line actually results, indicating deviations at both high and low light intensities. There is only one intensity level, characteristic for each emulsion, where the minimum exposure is required. At either greater or lesser values than this optimum intensity, more exposure is required to produce the same density. This extra exposure to produce the same density serves as a measure of the magnitude of the failure of the reciprocity law to apply to photographic materials.[30] (See Figure 16.)

Reciprocity failure is an ever-constant problem for those who use black-and-white or color photographic materials under varied exposure conditions. The failure of a modern, extremely high-speed film is shown in Figure 17 for the region of low exposure.

Intermittency Effect

The density given by an exposure consisting of a number of separate increments is usually different than the density produced by a single exposure of the same amount of light energy. This type of reciprocity failure has been called the intermittency effect of photographic exposure. Its discovery has been attributed to A. and L. Lumière in 1881, but W. de W. Abney[31] was

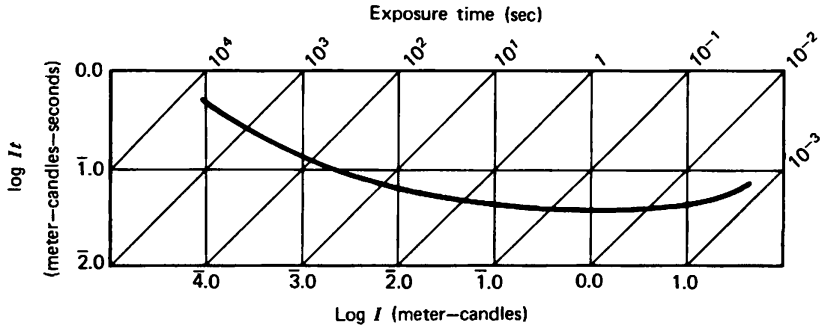


Figure 16. Graph showing reciprocity-law failure. [Eastman Kodak Company]

probably the first to study the effect quantitatively. Abney noted that an intermittent exposure was less efficient in forming latent image than a continuous exposure of equal energy. The exact effect depended upon the intensity of the exposing light, the number of separate flashes, and the ratio of the length of the light to dark periods.

Many investigators have studied the intermittency effect because of its importance in the design of a sensitometer, an instrument for exposing photographic materials for scientific study. The intermittency effect is often associated with the production of less density than that given by an equal-energy continuous exposure. More recent studies[32] have shown that when the light intervals of the intermittent exposure are about equal to the average rate of incidence of the photons upon the silver halide crystals, the intermittency effect disappears; that is, the intermittent exposure yields the same density upon development as would a nonintermittent exposure of the same duration and average intensity.

Intermittent exposures may form more density than an equal-energy continuous exposure when a sufficiently high intensity of illumination is used. At lower intensities a loss in density resulted. The gain or loss, or zero effect, of image density by intermittent exposure was explained by Raymond Davis[33] in the following manner:

> After extinguishing the illumination the latent image is subject to modification by two opposing influences, one tending to intensify it, the other to fade it—both rapidly decreasing with time. At the higher illuminations the resultant effect is a growth in density; at the lower, fading results. When the exposure is intermittent each interruption adds a part to the total growth or diminution of the image, but it is readily appreciated that, as the rest periods shorten, the change introduced by each interruption should diminish. Consequently, there should be a limit to the modification which an increase in the number of interruptions can cause.

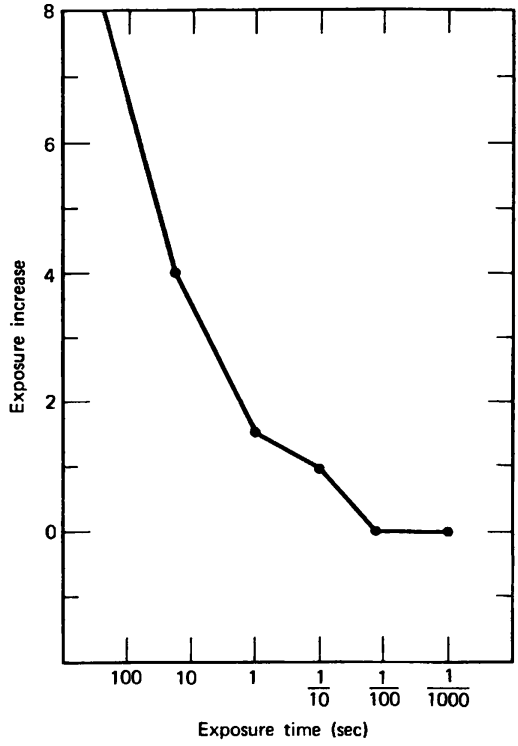


Figure 17. Reciprocity failure of Kodak Royal-X Pan film.

Intermittency failure is in the same direction as reciprocity failure but of a lesser magnitude. The loss of density given by the intermittency effect is associated with the underexposure region of the D–log E curve. In this region the curve produced by a continuous exposure rises more rapidly than the curve produced by an intermittent exposure. It was found by Clarence E. Weinland[34] that previous exposure to bring the latent image up to the beginning of the straight-line portion of the curve caused almost complete elimination of the intermittency effect. (See Figure 18.)

Reciprocity failure, and the associated intermittency effect, has significance for both the photographer and the scientist. At one time sensitometers used a constant-intensity light source that was modulated by a rotating sector wheel to vary the exposure. Because of the significant reciprocity failure that may be involved in such an exposing technique, this type of sensitometer has largely been supplanted by a sensitometer that is moderated in intensity by a continuous wedge or stepped tablet of varying densities. The exposure is

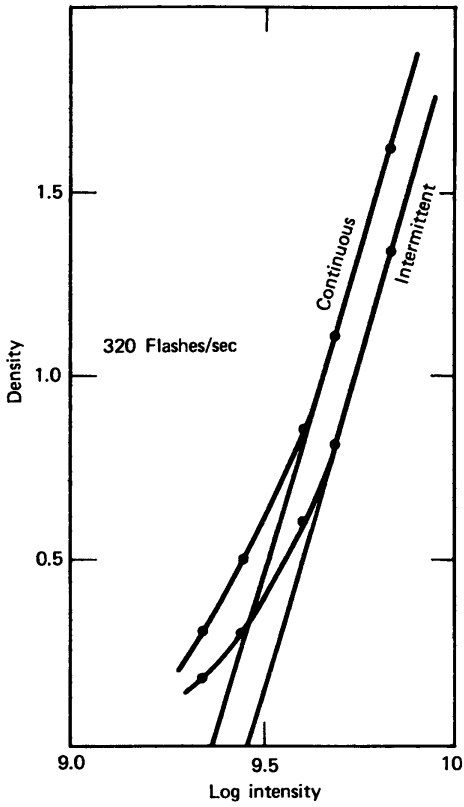


Figure 18. Characteristic curves with continuous and intermittent exposure, as determined by Clarence E. Weinland.[34]

continuous and of the same duration throughout the range of densities of the wedge or tablet.

The Measurement of Density

The density of the silver image is not an absolute quantity but depends upon the method of measurement of the opacity. The silver image of a negative is composed of fine particles of metallic silver which both absorb and scatter light passing through the negative. A portion of the incident light may pass directly through the negative. W. de W. Abney engaged in considerable controversy with F. Hurter and V. C. Driffield in the early 1890s concerning the value of various instruments to measure transmitted light.[35–38] Chapman Jones[39] later (1898) showed that scattered light could cause considerable discrepancies in the measurement of density, and that it was the scattered

light that made Abney's measurements differ from those of Hurter and Driffield.

In 1909 Andre Callier[40] studied the effect of scattered light upon density measurements, using parallel and diffused incident light. The ratio of

$$\frac{\text{density (measured by specular light)}}{\text{density (measured by diffused light)}}$$

was designated as Q by Callier and is often now referred to as the Callier Q factor. Q is always greater than one, as the specular density is always greater than the diffuse density. Callier found that although Q differed for each photographic material, its value was a constant for the density range of his work. The Q factor was later found not to be constant for all densities but to be a function of density. As the density of a silver deposit increases, the scattering of the incident light increases. The Q factor has been found to increase rapidly at the low values of density up to maximum, then decrease slowly.[41]

Because the amount of the silver deposit determined the amount of light scatter, the measurement has been difficult to standardize. Early density-measuring instruments usually had a sheet of opal glass in contact with the silver image of the negative. It was reasoned that light that was totally scattered by the opal glass would not be affected very much by the additional scattering of the silver image. This would minimize the variations of light scatter by different densities, but the values obtained depended upon the color, quality, and thickness of the opal glass. All light that passed through the photographic material should be measured. This was the conclusion of A. J. Bull and H. Mills Cartwright,[42] who proposed to use a hollow white sphere, called an integrating sphere, as a collector for all the light that was transmitted through the photographic material.

Density measurements by different instruments often produced different results. It would be desirable to have one method to yield standardized results so that densities could be compared throughout the world. A. M. Koerner and Clifton Tuttle[43] suggested that

> The necessary means for measuring the whole of the fluxes is available in the form of the integrating sphere. This device comprises simply a hollow, thin-walled sphere into whose periphery have been cut a pair of windows, located at approximately 90° from each other, and whose interior has been surfaced with some highly reflective and highly diffusive material such as magnesium oxide. Dimensions are immaterial, so long as the area of the apertures remains a negligible fraction of the whole surface of the sphere. It has been shown in the literature that the brightness of the interior of the walls of such a sphere is directly proportional to the amount of flux entering through the aperture, regardless of direction. Hence, if light from an external source is allowed to enter through one of the openings, the flux incident at the opening can be determined

by observing, through the second aperture, the brightness of the wall. If now a photographic image is laid against the first aperture and a second observation is made, all of the flux transmitted, either specularly or in a scattered manner, by the image, will have been determined, and by applying the Hurter and Driffield equation a value for the density of the image can be arrived at.

The integrating sphere of a density-measuring apparatus may measure all the incident light and all of the transmitted light, but the values obtained still depend upon the nature of the incident light. Practical density measurements may involve scattered (diffused), parallel (specular), or a combination of these two kinds of incident light. (See Figure 19.)

Three distinct kinds of density measurements are possible:

1. *Double diffuse density.* The incident light is diffuse, not specular, in nature. The measuring device is an integrating sphere that is in contact with the silver image. All the transmitted light, both scattered and unscattered, is measured.
2. *Diffuse density.* Essentially parallel rays of light are used to illuminate the silver image. As with doubly diffuse density measurements, the light collector measures all transmitted radiation. When a negative is placed in contact with a sheet of photographic paper and near parallel light is used to make an

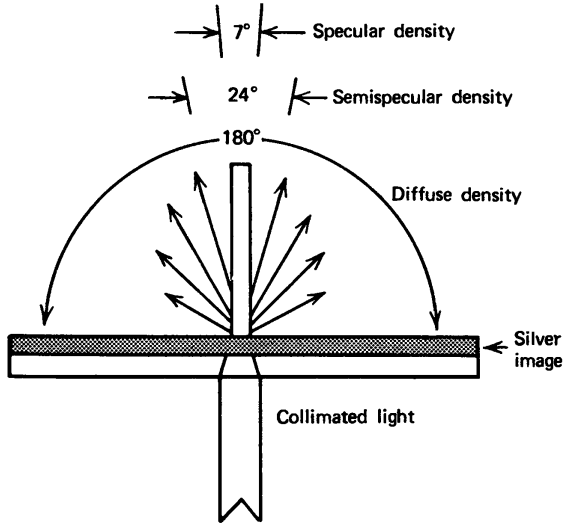


Figure 19. Means of collecting light after passing through a silver photographic image for making density measurements. [Eastman Kodak Company]

exposure, these photographic conditions of contact printing approximate the use of diffuse density of the silver image of the negative.

3. *Specular density.* When the light collector of the densitometer is moved back from the negative, only the direct rays of the light will be measured when the negative is illuminated with specular light. The incident light that was scattered will not be detected by the collector because the scattered light will diverge past the opening of the integrating sphere. Some of the incident light, though passing through the silver image, will not be detected by the densitometer. The amount of detected light will be less than the transmitted light, and the specular density will be higher in value than if both the scattered and direct light (totally diffuse density) were measured.

In projection printing with an enlarger having nearly parallel light (light collimated by condensers), the light emerging from a negative will consist of scattered and direct radiation. The light detector—the photographic paper—is at some distance from the negative, however, and the photographic emulsion will be affected primarily by the specular component of the transmitted light. The effective density of the photographic silver image is different for contact and projection printing because only part of the transmitted light is used for projection printing. Because the scattered light is not as effective with projection printing as it would be with contact printing, the contrast of the projection print will be higher than the contrast of the contact print, even though the same incident light illuminated the same negative in both methods of print making.

The density of the silver image of a photographic print is measured by reflectance. In this case the surface gloss plays an important part. If the silver image is illuminated with light at 45 deg to the print surface and the light detector is perpendicular (at 90 deg) to the surface, the effective reflection density will be measured. When the light detector is at 90 deg to the incident light, the specular reflection density will be measured. The total reflection density would be found by measuring the total light reflected in all directions and comparing the quantity with that of the incident light.

Covering Power

The efficiency of exposure is expressed in terms of density when the D–log E curve is constructed. But the amount of metallic silver in different photographic images may vary considerably, even though the images may have the same optically measured density. A measure of the efficiency of the metallic silver of an image to produce light-stopping opacity is called the covering power of the silver. Covering power is calculated by dividing the

grams of silver in a square decimeter of the original photographic material into the developed density given by that silver coverage; that is,

$$\text{covering power} = \frac{\text{density}}{\text{silver (g/dm}^2\text{)}}$$

The inverse of this relationship—the mass of silver divided by the density that it has produced—has been termed the photometric constant. Covering power, rather than its inverse, is now commonly used to study the conditions that produce maximum image blackness for the minimum amount of image silver, an obvious and desirable goal as the world's supplies of silver become less plentiful. Covering-power values depend not only on the properties of the silver deposit but also upon the method of measuring the density.[44]

Covering power is influenced by many factors. In 1928 S. E. Sheppard and A. Ballard[45] pointed out that covering power decreased with the time of development. This decrease was attributed to the increase in the average size of the developed silver particle with time of development. Many small silver particles of low mass are much more efficient than larger particles with relatively high mass per particle. Covering power was also found to increase with increased exposure, presumably by the selective action of exposure upon the larger silver halide crystals, which are more light-sensitive. Fog silver is much less effective (has lower covering power) in light-stopping action, and such silver may have a covering power only one-fifth that of silver formed by exposure and development. Even when all the silver halide in a film was developed to fog silver, the density of the maximum fog was much less than the maximum image density.[9]

Recent studies have indicated that the number of silver particles per unit area, their distribution in the emulsion layer, and their light-scattering and absorption characteristics primarily determine the density given after development of an ordinary emulsion layer. The interaction between exposure and development was summarized by G. C. Farnell and L. R. Solman[46] as follows:

> A fully chemically-developed silver-halide grain is a mass of silver filaments. The size of this mass, for a given size of silver halide grain, depends on the conditions of exposure and processing and also on certain properties of the emulsion. If the exposure is such as to produce large numbers of latent-image specks on each grain, e.g., a heavy high-intensity exposure, the developed grain may be very similar in size and shape to the undeveloped grain. With a low-intensity exposure producing only one or two latent-image specks, the developed grain is usually irregular in shape and larger than the undeveloped grain. Consequently, CP [covering power] may be higher for a low-intensity than for a high-intensity exposure.

Processing conditions play a vital role in determining the covering power of a developed silver image. The type of the developer, chemical or physical, influences the density given by the metallic silver, as the common non-filamentary silver particles given by physical development usually have less light-stopping power than the tangled mass of filaments given by chemical development. After the first stages of development in solution physical developers, the covering power of the developed silver decreases and the image becomes less neutral in color as the relative amount of solution physical development increases.[47] If the image is not neutral spectrally, covering power will depend to a degree on the wavelength of the light used to determine the image density.

The dependence of the covering power of the developed silver on the temperature and composition of the developer was studied by T. H. James and L. J. Fortmiller.[47] They reported that

During development, filaments may extend beyond the boundaries of the silver halide grain, providing the gelatin layer surrounding the grain can be readily penetrated. Swelling and softening of the gelatin would favor this penetration, whereas hardening would tend to prevent it. Accordingly, for a given degree of development, the filamentary silver formed by development of a given grain is less compact when the degree of swelling and softening of the gelatin is greater. Increased temperature promotes softening and swelling in the emulsions which have not been excessively hardened. Microscopic observations showed that the developed grains formed at the higher temperatures actually are larger, and hence have a less compact filamentary structure, since the mass of the silver is the same. The amount of gelatin washed out of the emulsion layer during processing also may be an important factor. An irreversible loss of density upon drying of a processed emulsion occurs with many materials, and this can be attributed to a compression of the filamentary structure by the contracting gelatin. The measurements made by Berry on the pressure exerted by the dry gelatin on the silver filaments suggest that the compression forces are weaker in the emulsion layer developed at the high temperature. The weaker force may be the result of the wash-out of part of the gelatin or may be associated with some other change occurring in the gel structure during the high-temperature development.

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