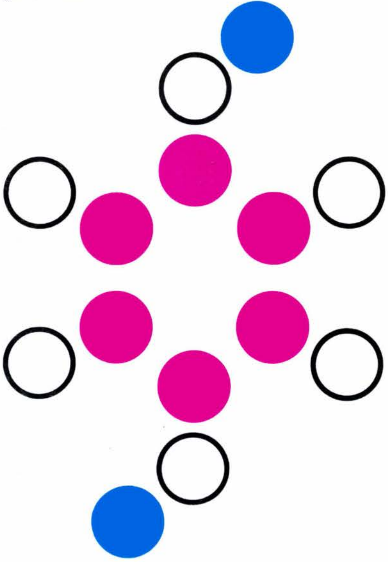
Photographic Chemistry

IN BLACK-AND-WHITE AND COLOR PHOTOGRAPHY

by George T. Eaton



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IN BLACK-AND-WHITE AND COLOR PHOTOGRAPHY

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MORGAN & MORGAN, Inc., Publishers
Hastings-on-Hudson, N.Y. 10706

Library of Congress Catalog Card No. 65-27034

Second Edition 1965
Printed in the United States of America

Preface

• This book is intended primarily for those who are active in photography or the photographic industry, who have had very little or no formal training in chemistry, physics or photographic theory. It is written for the purpose of giving these people a better understanding of the photographic process and, therefore, of the operations they are required to carry out in their everyday work.

The uses of photography multiply daily, particularly in industry and science, and better trained men are required. There is, consequently, a growing trend in the photographic industry, in the commercial and professional studios, in photographic laboratories and studios of all kinds to hire employees with photographic training and to urge or advise employees to attend night school or otherwise study photography.

A basic knowledge and understanding of photographic processing is one of the most important requisites in this new trend since all photographic material must be processed and since users of photographic materials are becoming more and more conscious of the importance of correct processing to insure better results, greater permanence, and more economical operation.

It is hoped that this rather informal discussion of the photographic process and particularly of processing will increase the reader's understanding. An effort has been made to simplify the chemical discussion in particular and it is hoped that those trained in the sciences may forgive some obvious liberties.

The organization and selection of material is based on the experiences of the author in conducting, for several years, a course for students in Photographic Chemistry at the Rochester Institute of Technology.

It should be of interest to the layman, to the amateur and professional photographer, to the industrial photographer, to the production people in the photographic industry and even to those trained scientists working in other branches of the photographic science. The book might be used as a text in high schools, in evening schools and extension courses designed to provide, on an elementary level, a better understanding of the photographic process.

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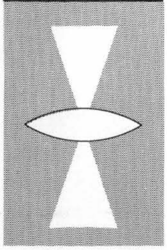
The Photographic Process



Photography is the process of producing a record by the action of radiant energy on a sensitized material and then treating this material so that the record will not disappear. It is actually what the literal meaning of the word "photography" indicates – the process of writing with light. The steps taken to accomplish this feat are grouped together and called the "photographic process."

- The steps in this process have been worked out over the years to make possible the beautiful color pictures, the black-and-white pictures, and the many photographic records used in science, business, and industry. No matter what kind of a record or picture is made, the basic operations of exposure, development, fixation, and washing are usually involved.

Exposure: Light is directed in some manner to act upon a light-sensitive material. Whether a subject is being photographed with a camera or some scientific data are being recorded, the light affects the photographic material to produce what is called the "latent image." This means that the light-sensitive material has been affected in such a way that it will be possible to obtain a visible picture or image by further treatment. Generally, the latent image is invisible to the naked eye.

Development: After exposure, certain chemical operations are necessary before the final picture is obtained. Development is the treatment of the exposed material in a solution known as the "developer" which converts the latent image to a "visible image."

Fixation: Following exposure, only part of the light-sensitive material has been affected by light. This portion, or the latent image, is made visible in the developer. The part which was not affected by light and not changed by the developer must be removed in order to produce a lasting image. Chemical solutions known as "fixing baths" are used for this purpose and the operation of using them is fixation.

Washing: It is necessary to remove the fixing-bath chemicals left in the material after fixation. Otherwise, in time these chemicals may affect the image and ruin a good picture. This removal is usually accomplished with running water.

Except in a few special applications, the processing is designed to produce a relatively permanent image which will remain in good condition for a long time. To accomplish this, the relationship between the fixing and washing operations is very important.

The simplest processing cycle used in making negatives, or prints from negatives, involves development, fixation, and washing. However, it is frequently desirable to include certain additional steps, such as use of an acid rinse bath between development and fixation, to allow more consistent control of the results and to reduce the carry-over of one solution into the next.

REVERSAL PROCESSING

The image formed in the above processing cycle does not look like the original subject because the whites of the subject are rendered black, and the blacks are rendered white. This is called a "negative," and it must be printed on photographic paper to produce a print image that does look like the original. There are applications of the photographic process in which it is desirable to obtain directly, without employing the printing operation, positive images that look like the original. This is so with amateur motion pictures in black-and-white and in color and with the production of still color transparencies and some color prints. To accomplish this requires considerable modification of the simple negative-type processing cycle. The technique is called "reversal processing."

Print

Negative

In negative processing, the exposed light-sensitive material is developed to give an image, and the unexposed and undeveloped material is fixed out. In reversal processing, it is the negative image that is removed by treatment in special baths, and the remaining light-sensitive material is then exposed and developed instead of being fixed out. The final picture, in this case, looks like the original. The use of water rinses is very important in this type of processing, because it is essential that all of the chemicals left in the photographic material after each treatment be removed in order to prevent interference with succeeding operations. Washing at the end of the reversal-processing cycle is necessary to remove any processing chemicals that could spoil the picture at a later date.

COLOR PROCESSING

The processing of color products is complicated by the fact that colored images must be formed during development and must not be destroyed by the succeeding operations. To prevent contamination of solutions and consequent poor color quality, carefully controlled water rinses are particularly important in the color-processing cycles.

PROCESSING CHEMISTRY

The chemistry of photographic processing is concerned with the reactions that occur during development, fixing, washing, etc.; with the adjustment of solution compositions; and with the control of conditions, such as temperature, that are needed to produce the desired results. Many of the details of processing chemistry apply equally to negative or reversal processing. And in color processing, although the developers are more complex, the same primary reactions are involved as in black-and-white processing. Consequently, it is possible to discuss separately each of the operations in the photographic process and thus avoid duplication in the discussions of processing—negative or reversal, and black-and-white or color.

In order to reach an understanding of these various operations, it is essential to know something about the composition of the light-sensitive materials and their reaction to light. A brief review of the early histories of chemistry and photography, which have culminated in our present-day photographic processes, will help in formulating a simple explanation of the chemical terms commonly used in photography.

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The Chemical History of the Photographic Process

The science of chemistry did not have its beginning until 1661, and photography until 1727.

• Through the years from 600 B.C. to 1661 A.D., there were many attempts to describe the composition of matter. Empedocles in 450 B.C. stated that matter consisted of four elementary materials: air, water, earth, and fire. Aristotle (384 to 322 B.C.) said that all matter contained a basic essence which was the carrier of four primary attributes of matter: hotness, coldness, dryness, and wetness. Combinations of these in pairs gave rise to the four elements of Empedocles. These ideas may appear foolish even to the laymen today, but there was no good definition or understanding of matter until 1661, when Robert Boyle defined "compounds" and "elements." He said "I mean by elements . . . certain primitive and simple, or unmingled bodies, which not being made of any other bodies, or of one another, are ingredients of which all those perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved." In other words, *elements are the simplest forms of matter, and they can combine to make compounds.*

During the 17th and 18th centuries, all learned men tended to dabble in chemistry: medical doctors, lawyers, teachers, and clergymen, hoping to discover something new, made experiments with the various available elements and compounds. Many of the basic theories in chemistry were evolved during this period. Some of the experiments which formed the basis of photography and the photographic process will be mentioned.

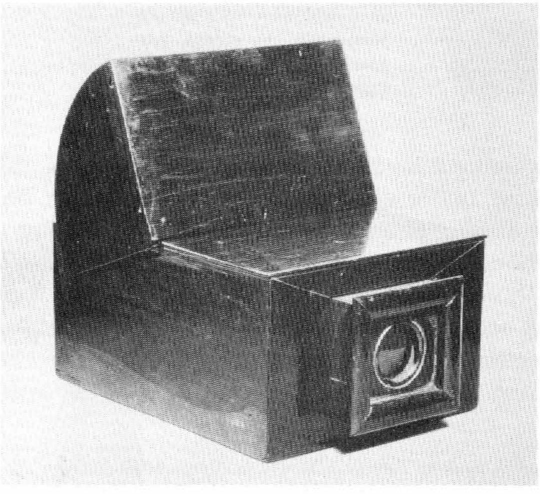
In 1727 T. H. Schulze was experimenting with compounds of silver. Actually, he was attempting to obtain an impression of stencils on surfaces coated with mixtures of chalk, silver, nitric acid, and other chemicals. He recorded that silver chloride, a compound consisting of the element silver combined with the element chlorine, was darkened by light. Silver chloride is one of the most important compounds used in photography.

Ten years later, Hellot was trying to make invisible inks. In one of his experiments he spread a solution of the compound silver nitrate on paper and noticed that it darkened when exposed to light.

In 1802, sixty-five years later, T. Wedgewood and Humphrey Davy were trying to produce silhouettes by the action of light in much the same manner as Schulze. They used silver nitrate solution coated on paper and tried to expose the coated paper in a "camera obscura." This was a lighttight box with a pinhole or a simple lens at the front to direct light onto the paper. They were unable to obtain an image, but it is significant that chemical and optical operations were brought together for the first time. A repeat test using silver chloride on paper in the camera obscura yielded an image, but the image did not last because no way was then known to remove the unused silver chloride so that it would not darken and obscure the image. Incidentally, the camera obscura, used by artists to trace an image on a ground glass, was first described by Leonardo da Vinci in the 16th century.

It was not until 1837 that J. B. Reade discovered the ability of sodium thiosulfate, or "hypo," to remove the light-sensitive chemicals from the unexposed areas in a negative or print. Hypo reacts with the silver compound to form new compounds that can be removed by bathing in water. The solution of hypo is a "fixer" or "fixing bath."

About this time Fox Talbot suggested that a special solution might be found which would generate or develop an image on the sensitized surface after a very short or weak exposure. In other words, the



Camera Obscura. The image was reflected from a mirror onto a ground glass screen shielded by a raised hood. By laying thin paper over the glass, an artist could trace the image.

visible image would be produced chemically instead of entirely by prolonged exposure to light. His own success in these experiments was announced in 1841. This process produced a "negative" in which the dark areas of the subject were reproduced light, and vice versa. The image was also reversed left to right. "Positives," in which tones are in the same relationship as in the subject, were made from the negative. This is the "Calotype" process* and was the forerunner of modern photography. For the first time, an exposed light-sensitive layer could be processed by development and fixation to produce a picture that could be kept for some time.

A faster process was desired, and further experiments resulted in Scott Archer's wet-plate process (1851). He made a suspension of silver chloride in nitrocellulose, coated it on glass plates, exposed it immediately while wet, and developed it. The coating was made on glass plates instead of paper, and though inconvenient, produced finer results. The process is still used by a few groups in the graphic arts trade.

A wet-plate photographer with his heavy pack. It was necessary to carry a portable darkroom so that the plate could be coated, exposed, and processed in rapid order before it dried.

The cumbersome equipment involved in the use of wet plates was inconvenient, but nothing better was available until after 1870. Dr. Maddox described the making of an emulsion by forming silver bromide in a gelatin solution. This emulsion could be coated and dried before use. Although this emulsion was first sold in bulk, emulsion-coated dry plates were soon commercially available. The principles underlying the preparation of current photographic emulsions are not greatly different from those applying to the making of the early dry plates.

**A group of original Calotype prints made by Talbot can be seen in George Eastman House, Inc., Rochester, N. Y.*

William Henry Fox Talbot

Frederick Scott Archer

EARLY CHEMISTRY

During this development of the photographic process, clarification of some early chemical theories occurred. Atoms, elements, and compounds were defined. The vague theories of the Greek philosophers and the alchemists were discarded by 1803. In 1808 Dalton, a schoolteacher, claimed that atoms are definite, concrete grains of matter, indivisible and unaffected by the most violent chemical change. Atoms of the same kind grouped together constitute an element. There are different kinds of atoms and, therefore, different elements. When different atoms combine, the result is a "molecule," and groups of the same molecule constitute a "compound."

Materials such as copper and sulfur are elements. Copper is a reddish tough metal that conducts heat and electricity. Sulfur is a yellow crystalline powder that burns freely in air, is not metallic, and does not conduct electricity. However, when copper filings are heated with "flowers of sulfur," the two elements combine chemically to form a compound, copper sulfide, which is black, nonmetallic, does not conduct heat or electricity, and does not burn in air. It does not have any of the properties or characteristic appearance of either of its elements.

Another familiar example is the "tarnish" produced on silverware. Hydrogen sulfide gas (which has the smell of rotten eggs) from illuminating gas and coal produces the tarnish because the element sulfur in the gas reacts with the element silver to produce the brownish-colored compound silver sulfide on the surfaces of the silverware.

Another interesting example is ordinary table salt, which the chemist calls "sodium chloride." Both of its elements, sodium and chlorine, are extremely reactive and dangerous individually, but when combined chemically they produce harmless table salt. The fact that new compounds formed by chemical reaction have properties quite different from those of the original substances makes processes like photography possible.

By the time the dry plate was a commercial reality, atoms, elements, and molecules had been defined. However, it was not understood how atoms were held together in molecules, why certain elements reacted with each other, nor how atoms were arranged in molecules. These problems were not explained until after 1897. This is significant because an explanation of how and why the photographic process works was impossible until the fundamental chemistry was understood. Nevertheless, the practical testing of various chemicals for use in emulsion manufacture and processing progressed, and many advances in the practice of photography were made by trial and error.

COLOR PHOTOGRAPHY

Shortly after the introduction of Scott Archer's wet-plate process, the first photograph in color was demonstrated – on May 17, 1861 – by Clerk Maxwell before the Royal Institution in England. A good picture was not obtained, but a color process was described. Three photographic plates were exposed through three differently colored solutions (filters, see Chapter IV), and after processing and printing, the positive images were projected and superimposed onto a screen using the same filters in front of three projectors.

Louis Ducos du Hauron, a Frenchman, became interested in this phase of photography about 1859 and described his first color method in 1869. He outlined the basic principles of all the color processes which have since been invented. Independently, and at the same time, Charles Cros described several processes. Although the principles were clearly defined for several color methods, no commercially practical process was possible because of inadequate photographic materials. The advent of silver halide-gelatin dry-plate emulsions and the discovery of emulsion sensitizers (see Chapter IV) assisted greatly in the development of color processes.

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Ag + Br

The Photographic Emulsion

The photographic emulsion is the light-sensitive layer coated on a glass, paper, or film support. It consists essentially of light-sensitive silver compounds dispersed uniformly in gelatin.

• In the early history of the photographic process, the silver compounds — specifically, silver chloride, silver bromide, and silver iodide — were found to be particularly sensitive to light. These compounds are formed in a special way in the manufacture of photographic emulsions. They are made by reacting certain chemicals under special conditions. In order to show how they are formed, it is easier to use chemical language.

There are 96 currently known chemical elements. Chemists have developed a set of abbreviations so that each element may be represented by a characteristic chemical-shorthand symbol. For example, the symbol for silver is Ag, from the Latin *argentum;* chlorine is Cl; sodium is Na, from the Latin *natrium;* and so on. When two or more of these elements combine, a compound is formed by a chemical reaction which is described by means of a chemical equation as follows:

$$\underset{\text{sodium}}{\mathrm{Na}} + \underset{\text{chlorine}}{\mathrm{Cl}} = \underset{\substack{\text{sodium chloride}\\ \text{(table salt)}}}{\mathrm{NaCl}}$$

This kind of reaction is known to chemists as a "combination," and the reverse kind, as a "decomposition." This equation also means that a certain amount of sodium reacts with a certain amount of chlorine in the ratio of one atom of sodium to one atom of chlorine (see page 29).

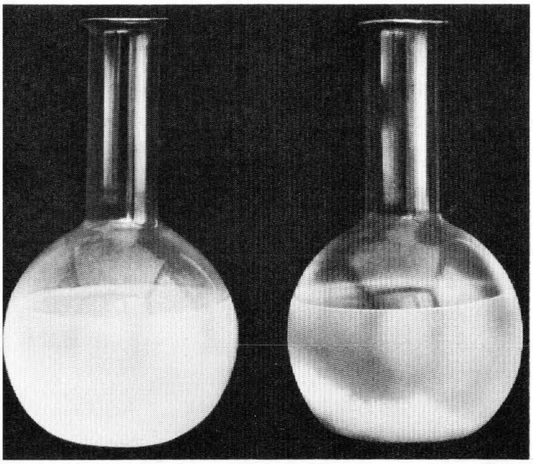
Similar equations can be used to describe the more complex reactions between two or more compounds. These reactions are known as "double-decomposition" reactions. For example, when the compounds silver nitrate and potassium chloride are each dissolved in a separate quantity of water and then the solutions are mixed, the following equation tells the story in chemical shorthand:

$$\underset{\substack{\text{silver}\\ \text{nitrate}}}{\mathrm{AgNO_3}} + \underset{\substack{\text{potassium}\\ \text{chloride}}}{\mathrm{KCl}} = \underset{\substack{\text{silver}\\ \text{chloride}}}{\underline{\mathrm{AgCl}}} + \underset{\substack{\text{potassium}\\ \text{nitrate}}}{\mathrm{KNO_3}}$$

To understand this equation, a new idea must be introduced at this point. Certain elements hang together very strongly in special combinations known as "radicals." A radical acts as a unit in many chemical reactions in a similar manner to the individual elements. For example, in silver nitrate in the above equation, the combination NO_3, which consists of one atom of nitrogen and three atoms of oxygen, is the nitrate radical. In many reactions it acts as a unit, much like a single element, for example, silver, chlorine, or potassium.

The silver chloride (AgCl) is underlined to indicate that it is precipitated because it is comparatively insoluble in water. This is the basic reaction in the manufacture of the photographic emulsion. If potassium bromide (KBr) or potassium iodide (KI) were used in the reaction, silver bromide (AgBr) or silver iodide (AgI), respectively, would be formed. These three silver compounds — silver chloride, silver bromide, and silver iodide, are known as "silver halides" and form the light-sensitive constituents of photographic emulsions.

When water solutions of silver nitrate and potassium chloride are mixed, silver chloride forms very quickly and settles to the bottom. It is lumpy and in the form of large-size crystals which cannot be spread in a smooth layer on a support. Silver choride in this form is not very sensitive to light. If the reaction could be slowed down so that the silver choride crystals would be smaller and more uniform in size, the sensitivity to light would increase. This is actually accomplished by using gelatin in the water solutions. In addition to having their size controlled, the halide crystals must be uniformly dispersed



The silver chloride formed in the flask on the left is held in suspension by gelatin. In plain water, without gelatin, the silver chloride settles to the bottom, as shown on the right.

in the solution of gelatin. The uniform suspension of the silver halide in the gelatin, called the "photographic emulsion," makes it possible to coat the emulsion on suitable supports (glass, paper, and film) in layers of uniform thickness and having uniform sensitivity to light. When these silver salts are produced in the presence of gelatin, they are also more sensitive to light. Further experimentation revealed that this sensitivity could be increased still further by the addition of other chemical compounds (known as "sensitizers") to the mixture of silver salts and gelatin.

GELATIN

Since gelatin is so important in the manufacture of photographic emulsions, and influences the processing of the emulsion so much, some of its characteristics will be discussed.

The 96 elements mentioned previously enter into hundreds of thousands of combinations to form as many different compounds. These compounds have been broadly divided into two types, called "inorganic" and "organic." Both types occur in nature, and many are made or synthesized in the chemical laboratories. The term "organic" was originally applied to compounds formed in the organs of plants and animals. They are also characterized as those which burn, and include, for example, sugar, starch, and alcohol. They are composed chiefly of the elements carbon (C) and hydrogen (H), frequently with oxygen (O), and sometimes contain nitrogen (N), sulfur (S), or other elements in various combinations. On the other hand, inorganic compounds, in general, do not burn. They are composed of elements other than carbon, e.g., copper, silver, gold, iron, sodium, sulfur, chlorine, bromine, and so on. These will be discussed later in Chapter V.

Gelatin is a very complex organic material obtained from animal skins and hoofs. It is a compound of carbon, hydrogen, oxygen, nitrogen, and sulfur in a specific arrangement, but a molecule of gelatin is so complex that the exact proportions of the elements it contains are not known. Its properties depend upon its source and previous history. This is particularly true in regard to its photographic properties.

Photographic gelatin is very carefully prepared and is actually purer than the well-known cooking gelatins. Generally, gelatin is obtained from the left-overs in slaughterhouses, such as the hoofs and hides. Photographic gelatin is obtained from very carefully selected hides and ears of calves. It is even important to consider the kind of feed which the calves have eaten. Certain weed seeds, e.g., mustard seed, common in some areas, will change the chemical characteristics of the gelatin obtained from the calf hides just enough to affect its use in photographic emulsions.

The selected hides and ears are treated in boiling water to remove any dirt. They are then soaked for as long as two months in a lime ("liming") solution to remove hair, fat, and albumen; washed; and finally, treated in a dilute acid to neutralize* the lime ("de-liming"). The resulting material is called collagen which is the immediate source of the gelatin.

Collagen is then treated slowly over a considerable period of time and under specially controlled conditions to break it down gradually into gelatin. If the treatment is too vigorous, there is produced a poor-quality gelatin which is not suitable for photography.

It was mentioned above that gelatin was extremely important in the manufacture of photographic emulsions because it permitted a slower reaction between the chemical solutions used in forming the light-sensitive emulsion and produced a uniform suspension of very small silver halide crystals. Compounds, such as gelatin, which form viscous solutions, jellies, or noncrystalline solids (e.g., glass) are known as "colloids." Other well-known colloids are glue, agar-agar, albumen, and collodion. Because of its particular combination of chemical and physical properties, the most important of which are listed below, gelatin has proved to be the most satisfactory colloid for photographic emulsions.

(1) Gelatin is a colloid which keeps the silver halide particles uniformly dispersed and is important to the finished photographic film or paper.

(2) Dry gelatin is stable for long periods of time and, as a result, permits reasonably permanent products both before and after processing.

(3) Gelatin has no chemical effect on the silver halides in the coated emulsion (only during emulsion making).

(4) Gelatin is permeable enough to allow penetration of the various processing solutions through its structure without destroying its toughness or permanence.

(5) Gelatin can be handled quite simply and in a reproducible manner.

**Lime is alkaline and feels slippery like soap, while acetic acid is the acid which gives vinegar its sour taste. Acid will* kill *alkali, and vice versa. When all of the lime present is just* killed, *it is said to be "neutralized." See page 48 for further discussion.*

It was stated that gelatin is a very complex organic material containing carbon, hydrogen, oxygen, nitrogen, and sulfur. When gelatin is analyzed in a chemical laboratory under certain special conditions, it will break down into smaller units which can be postively identified. These are the well-known amino acids. The amino acids have two special groupings of elements in each molecule. Glycine, the simplest amino acid, can be written in chemical symbols as:

$$\underset{\text{I}}{NH_2} - CH_2 - \underset{\text{II}}{COOH}$$

The groups or arrangements marked "I" and "II" occur in all amino acids and thus are known to occur repeatedly in the complex gelatin molecule. The NH_2 is called the "amino group" and the COOH is called the "carboxyl group." These groups will be of special interest later.

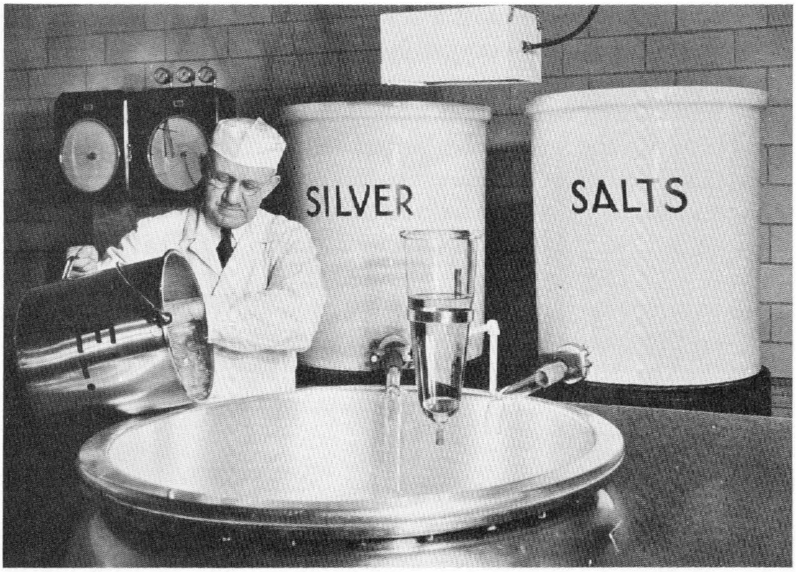
MANUFACTURE OF EMULSIONS

It is interesting to know about the steps followed in the manufacture of photographic emulsions. The equation describing the basic chemical reaction is:

$$AgNO_3 + KCl = \underline{AgCl} + KNO_3$$

When making a simple emulsion, a 10 percent solution of silver nitrate is added slowly and with vigorous stirring to a second solution containing gelatin and potassium chloride. Exceedingly fine silver chloride crystals are formed gradually, but the emulsion produced at this stage is not very sensitive when exposed to light. This operation is usually performed under a dim red light.

This emulsion, or suspension of silver halide in gelatin, is then ripened or digested to make it more sensitive to light. This is done by heating the emulsion to a definite temperature, usually around 90 F, and maintaining it there sometimes for several hours. Even though the silver halide crystals formed at first are very fine, there is some variation in size. During ripening, the smallest crystals are dissolved and then re-deposited on some of the larger crystals. As a result a larger and probably more uniform crystal size is obtained. But more important is the fact that the sensitivity of the crystals to light has been increased considerably because the whole reaction took place in the presence of gelatin. Usually, just before the ripening process is completed, more gelatin is added. The nature of this gelatin can have a very definite effect on the final sensitivity of the silver halides. After the ripening treatment, the whole solution is cooled to a stiff jelly.



In the manufacture of photographic materials, one of the first steps is the mixing of solutions of gelatin, silver nitrate, and a soluble halide to produce an emulsion.

The jelled emulsion is then shredded, leaving it in the form of "noodles." These noodles can then be washed to free the emulsion of unwanted chemicals, such as any excess potassium salts. Jelled emulsion can be stored in the dark at a low temperature until required for production of the final product.

The noodles are remelted and kept at an elevated temperature for some time, causing a rapid gain in speed and contrast. This is the second ripening or digestion of the emulsion. The changes that occur in this stage are controlled by the particular gelatin added at the end of the first digestion or ripening. After sufficient ripening, other materials, including hardening agents, sensitizers, and so on, are added to the emulsion. The emulsion is then coated onto a suitable support.

Hardening agents are chemical compounds added to the emulsion to make the gelatin tough and more resistant to swelling and softening in the subsequent handling and processing operations. Sensitizers are special organic chemicals added to increase the sensitivity of the silver halides to certain colors of light. The chemistry of these compounds is too complex to discuss here, but the effects they have in emulsions will be described later.

GENERAL TYPES OF EMULSIONS

The equation representing the formation of the light-sensitive silver halides indicates that there are as many atoms of each element on one side of the equation as on the other side, for example,

$$AgNO_3 + KCl = \underline{AgCl} + KNO_3$$

When the exactly equivalent quantities of silver nitrate and potassium chloride required by the equation are used, the emulsion produced is not very good for practical use. It is necessary in manufacturing to use an excess of one or the other of the chemicals, but two entirely different types of emulsion are then produced, depending upon which chemical is in excess.

If the amount of silver nitrate is greater than that needed to react with all of the potassium chloride, a PRINT-OUT emulsion is produced. This type of emulsion is usually exposed to a very high-intensity light source for sufficient time to "print-out" the image. No processing is required. The reddish-colored portrait proofs often used by professional photographers are typical of a print-out material.

If the amount of potassium chloride is greater than that needed to react with all of the silver nitrate, a DEVELOPING-OUT emulsion is obtained. This is the conventional type of emulsion exposed in cameras, enlargers, and printers. It requires only a relatively short exposure followed by chemical development.

Developing-out emulsions are used on both negative and print materials. In general, the negative emulsions are washed, while in the form of noodles, to remove all excess chemicals. Frequently, the paper emulsions are not washed.

Of course, there are marked differences between various developing-out emulsions, depending upon the particular silver halide or halides used. A very general classification of photographic materials can be made on the basis of their relative sensitivity to light, as shown in the chart below. The sensitivity of the halides to light increases in

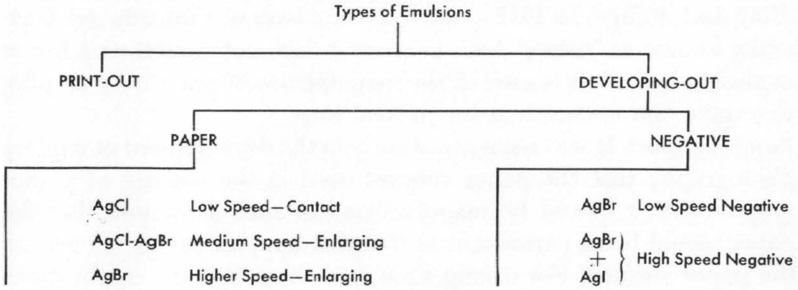


FIGURE 1

the order chloride, bromide, and iodide, so that a silver bromide emulsion is "faster," or more sensitive to light, than a silver chloride emulsion. Consequently, most negative materials are silver bromide with or without a small percentage of silver iodide, and paper materials are either silver chloride, silver bromide, or a mixture of the two.

SUPPORTS FOR COATING PHOTOGRAPHIC EMULSIONS

The most commonly used supports are, of course, glass, film base, and paper. Some special products are made by coating emulsions on tracing cloth, metal, pressed woods, and so on. However, these are used in very special applications of photography and will not be discussed here.

Glass for Photographic Plates. Glass was first used as a support for light-sensitive silver halide emulsions in the Wet Plate Process of Scott Archer introduced in 1851. It was also used for coatings of the first gelatin emulsions introduced by Dr. Maddox in 1870.

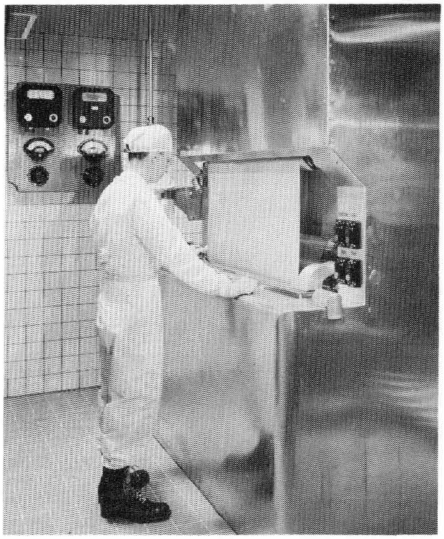
Carefully selected window glass is used in the regular production of photographic plates. It is selected for flatness and freedom from flaws which might impair the uniform transmission of light through it.

Film Base. Although glass plates are still used in large quantities in some photographic applications, for general use they have largely been replaced by flexible paper and film supports. A flexible support was required and developed as a necessary part of a simple box- camera system envisioned and made commercially available by George Eastman. In the first Kodak box camera, the roll of light-sensitive material was emulsion coated on paper. In 1889 the first transparent film base coated with emulsion was made available.

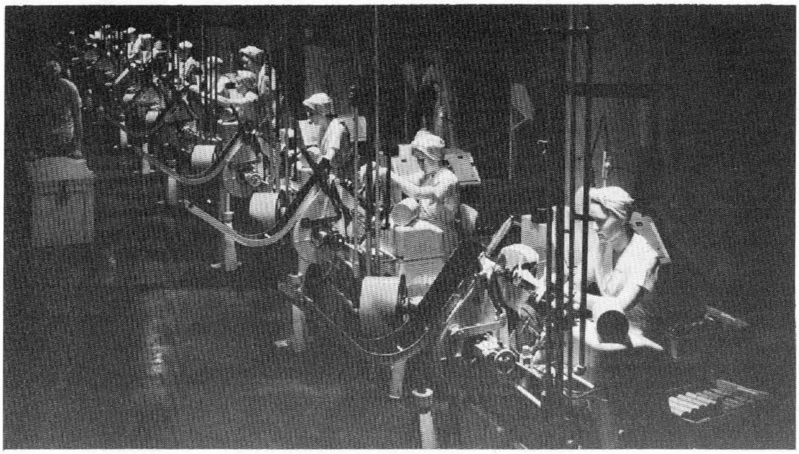
Film base is made from cellulose obtained from wood pulp and cotton linters by treating them with appropriate chemical compounds. The first such film base was essentially cellulose nitrate. This substance is, unfortunately, very inflammable, and its use constitutes a serious fire hazard unless special precautions are taken in its handling and storage. In 1912 a new-type film base was introduced. Generally known as "safety" base because it does not constitute a fire or explosion hazard, it is used in the manufacture of practically all photographic film materials at the present time.

Paper Support. It was recognized early in the development of modern photography that the paper support used in the making of photographic prints should be manufactured in such a manner that the paper would be as permanent as the photographic image formed on the paper surface. For a long time, and even in some applications today, paper made from rags was considered the most permanent. However, the photographic manufacturers initiated a long-term research program to produce a paper made from wood pulp that would be as permanent or more so than "rag" stock. The Eastman Kodak Company, in co-operation with wood-pulp producers, developed a technique for making pulp that would meet the specifications for a permanent photographic paper support. Practically all photographic paper stock manufactured today is made from wood pulp.

Right — Emulsion being coated on film base. Work areas must be kept meticulously clean so that no dust or other foreign matter can become imbedded in the emulsion.



Below — One of the air-conditioned rooms where film is spooled at the Eastman Kodak Co. This picture was taken in the dark with infrared film and invisible infrared light.



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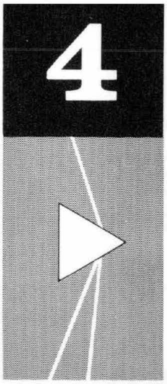


The Reaction of Photographic Emulsions to Light

The making of pictures is dependent upon the fact that the silver compounds are sensitive to light. But what is light and how does it affect the photographic emulsion?

• When photographic materials – plates, films, and papers – are exposed in cameras, enlargers, or printers, the silver halides in the emulsions are affected by the exposing light to form an invisible latent image. Before it is possible to describe what happens during exposure of the silver halides, it is necessary to consider briefly the nature of light itself.

NATURE OF LIGHT

The available evidence indicates that light consists of waves that travel at 186,000 miles per second. One form of transmission of energy by wave motion can be simply demonstrated by fastening one end of a length of rope to a post and then rapidly moving the free end up and down. A "wave" will be observed to run along the rope. The distance from crest to crest is called the "wavelength."

White light actually consists of mixtures of waves of various lengths. When light passes from air into glass, the light rays are bent, or refracted, and the amount of bending has been found to depend on the wavelength of the light. When a beam of white light is passed through a prism, a band of colors, known as a "spectrum," is formed.

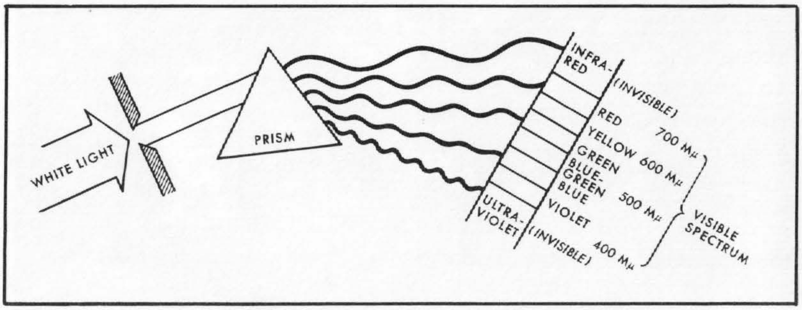


FIGURE 2 Formation of the spectrum

The colors range from blue through blue-green and green to green-yellow to orange to red. The prism experiment proves that white light is a mixture of different colors of light, each having its own particular wavelength, because the amount of bending of the rays is different in each case. Therefore, color depends on the wavelength of light. The relative wavelengths of blue, green, and red light can be indicated as shown in Figure 2.

The wavelengths of light can be measured accurately and are usually expressed in either millimicrons or angstrom units. One millimicron, abbreviated mμ, is one millionth of one millimeter, while one angstrom unit is one tenth of this, i.e., one ten-millionth of one millimeter. The spectrum can be represented by a chart on which the wavelength of the different colors of light is indicated, most often in millimicrons. This spectrum of color is called the "visible spectrum" since these colors are visible to the human eye.

The visible spectrum, which includes the approximate wavelength range of 400 to 700 millimcirons (mμ), is, however, only a small part of a much longer spectrum known as the "electromagnetic spectrum" (Figure 3). Some radiations, such as ultraviolet rays, x-rays, and gamma rays, have wavelengths shorter than 400 mμ, while infrared and radio waves have wavelengths longer than 700mμ. Even though these radiations are invisible, photographic emulsions are sensitive to some of them. All photographic emulsions are sensitive to the ultraviolet, x-ray, and gamma radiations. Certain special emulsions will record in the shortest ultraviolet wavelength range.

For many applications of light, and photography in particular, it is convenient to divide the visible spectrum into three regions (blue, green, and red). Separation of these three regions can be demonstrated readily by placing suitably colored pieces of glass over the lens on a projector. When a piece of red glass is used, the light projected onto a white screen is red in color. The red glass has transmitted the red light and absorbed the blue and green light. In a similar manner, a red object is red because the object absorbs the blue and green light and reflects only the red light.

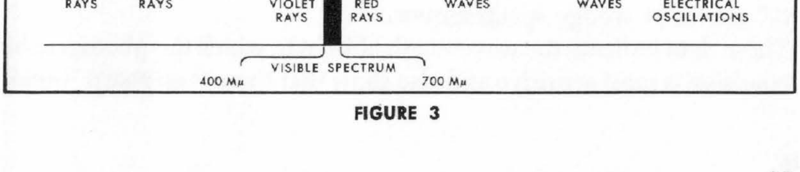


FIGURE 3

EXPOSURE OF SILVER HALIDES IN AN EMULSION

The silver halides in a photographic emulsion behave toward light in a manner somewhat similar to that of a colored object. This means specifically that the halides are capable of absorbing only certain wavelengths of light. When this happens, the absorbed light produces within the silver halide crystals chemical reactions which form the latent image which, in turn, is later made visible by development.

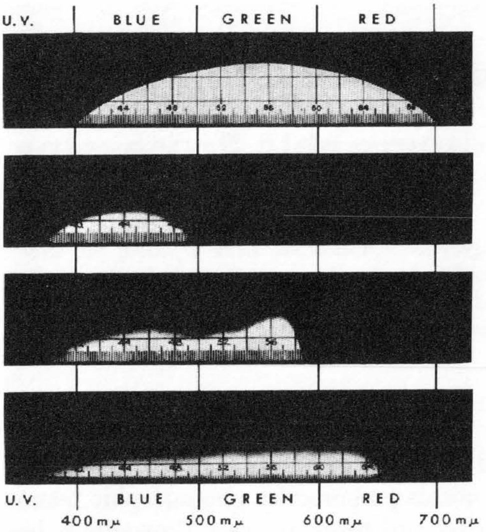
The absorption of light by the silver halides is limited to only a part of the visible spectrum. Silver chloride, for example, absorbs the wavelengths of light in the blue region of the visible spectrum up to approximately 500 mμ. Silver bromide and silver iodide absorb up to about 525 mμ and 550μ, respectively. If commercial emulsions contained only pure silver halides, then photographic materials would record only the blue light reflected from any subject being photographed. These emulsions would be described as "blue-sensitive."

Actually, most subjects display a variety of colors, and it is desirable to show these colors as shades of gray of proper brightness in a black-and-white photograph. It has been found that, to make the silver halides responsive to more wavelengths of light, certain complex organic chemicals can be added to the photographic emulsion during manufacture. In other words, the sensitivity of the emulsion can be extended into the green and red regions of the visible spectrum. These improvements in manufacture give rise to two general classes of photographic materials known as "orthochromatic" and "panchromatic." The organic chemicals used are known as "sensitizers," and the increase in sensitivity of the emulsions to additional parts of the spectrum is called "optical sensitizing." Several series of sensitizers make emulsions sensitive to the wavelengths of light in the green portion of the spectrum. All conventional photographic materials are blue-sensitive because they contain the silver halides.

In color photography, emulsions that are sensitive to all wavelengths of the visible spectrum are required in order to record all colors in the subject through the blue, green, and red filters.

The sensitizers used to make emulsions orthochromatic, for example, do not all produce in the emulsion the same sensitivity to light. The relative effects of different sensitizers can be determined experimentally and the results shown by means of either "spectral-sensitivity" curves or wedge spectrograms.

These data indicate the wavelength of light to which the photographic emulsion is most sensitive and also show that there is no sharp "break"



SENSITIVITY OF THE EYE
Approximate sensitivity of the normal eye.

NON-COLOR-SENSITIZED
Have only the ultraviolet and blue-violet sensitivity inherent in every silver halide emulsion.

ORTHOCHROMATIC
Ultraviolet, blue, and green sensitivity.

PANCHROMATIC
Sensitivity closely approximating that of the eye.

FIGURE 4 Wedge spectrograms showing color sensitivity of film sensitizing types to tungsten light.

between this wavelength and immediately shorter or longer ones. Wedge spectrograms provide the best general information about the sensitivity of emulsions and are widely used in literature, such as data sheets, describing the characteristics of products.

There are organic sensitizers which will make emulsions sensitive to parts of the infrared wavelength range. Some of them can extend the sensitivity to as far as about 1250 mμ. Many of these infrared-sensitive emulsions are extremely important in aerial survey, in astronomy, and in other technical and scientific applications of photography.

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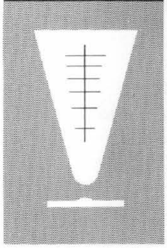


Solutions and Chemicals in Photographic Processing

When the photographic emulsion has been exposed, the latent image is made visible by development. Special developer solutions are required. Important properties of some of the chemicals used in developers and other processing solutions are discussed.

• Processing solutions can be mixed from the separate chemicals combined as recommended in published formulas, or they can be made with packages of chemicals prepared by photographic manufacturers. Packaged developers and fixers are very dependable because they are mixed and packaged in large volume and under closely controlled conditions. These proprietary products have become very popular in recent years because of their uniformity from package to package, the convenience in mixing provided, and the relatively low cost, especially in those cases where large volumes of exposed material are involved. Regardless of how the solutions are prepared, knowledge of the chemicals is important.

In Chapter III it is shown that two or more different elements may combine to produce chemical compounds. Each of these chemicals has different characteristics, according to the particular combination of elements it contains. However, some of them are quite similar in their properties and reactions to a number of other closely related chemicals. They can be grouped into several broad classes on this basis.

The elements can be classified broadly into two groups: metals and nonmetals. The latter group contains a number of elements which are gases at normal temperature and pressure. The elements of greatest importance in photography are shown in Table I.

In any chemical reaction, certain quantities or weights of elements and compounds are involved. Each element is composed of atoms of the same kind. It is possible by precise methods to determine the average relative weight of the atoms of each element. This average weight is known as the *atomic weight* and is different for each element. For example, the atomic weights of sodium, carbon, chlorine,

TABLE I

METALS			NONMETALS		
Element	*Symbol*	*Atomic Weight*	*Element*	*Symbol*	*Atomic Weight*
Sodium	Na	23	Carbon	C	12
Potassium	K	39.1	Boron	B	10.8
Calcium	Ca	40.08	Sulfur	S	32
Iron	Fe	55.84	Iodine	I	126.9
Copper	Cu	63.57	Bromine	Br	79.9
Silver	Ag	107.88	*GASES*		
Gold	Au	197.2	Hydrogen	H	1.008
Platinum	Pt	195.23	Nitrogen	N	14
Aluminum	Al	26.97	Oxygen	O	16
Mercury	Hg	200.6	Chlorine	Cl	35.5

and silver are respectively 23, 12, 35.5, and 107.88, expressed on a scale which starts with hydrogen at 1.008.

In the reaction between sodium and chlorine, sodium chloride was formed according to this equation:

$$Na + Cl = NaCl$$

Each atom of sodium combines with one atom of chlorine. The weights of the two elements involved are in proportion to their atomic weights, namely 23 for sodium and 35.5 for chlorine. These weights of the two elements will always react with each other to form sodium chloride; or conversely, the sodium chloride will always have the two elements present in exactly the same ratio of 23 to 35.5. These weights can be measured in grams, ounces, or any other measure, as long as the correct proportion of the quantities is maintained. Similarly, the various other known compounds are formed from combinations of the atoms of different elements in some definite ratio. For example, water, which is H_2O, always has a simple combination of two atoms of hydrogen to one atom of oxygen.

When the sodium and chlorine react, molecules of sodium chloride are produced, and the sum of the weights of the atoms, or 58.5, is the molecular weight of sodium chloride.

Atoms do combine in ratios other than one to one to form compounds. For example, in the case of water, two atoms of hydrogen always combine with one atom of oxygen. The quantities of the two elements involved are in proportion to their atomic weights, that is, 2.016 for hydrogen (twice the atomic weight of hydrogen) and 16.0 for oxygen. The molecular weight of water is therefore 18.016.

Similarly, radicals, such as the nitrate, NO_3, react as a unit. In the formation of sodium nitrate, one atom of sodium combines with one nitrate radical, and the quantities involved are the atomic weight of 23 for sodium and the total weight of 62 for the nitrate radical, which is the sum of the atomic weight of 14 for nitrogen and three weights of 16 for oxygen. Thus, the molecular weight of sodium nitrate is 85.

The equation for making a simple emulsion was

$$AgNO_3 + KCl = AgCl + KNO_3$$

To determine the quantities of silver nitrate and potassium chloride required for the reaction as expressed by the equation, the molecular weights of the compounds are calculated by adding the atomic weights of the elements involved.

The ratios in which the atoms of different elements combine have been determined by analysis of many known compounds, and as a result, it is possible to indicate the reactivity of an element with other elements. This characteristic of the element is called "valence."

TYPES OF COMPOUNDS

Oxides are compounds formed by the combination of oxygen with other elements. For example, sulfur and oxygen combine to form sulfur dioxide, that is,

$$S + O_2 = SO_2$$

and sulfur dioxide can react with more oxygen at an elevated temperature (400 F) to produce sulfur trioxide, that is,

$$2\ SO_2 + O_2 = 2\ SO_3$$

Similarly, sodium can react with oxygen to form sodium oxide, that is,

$$4\ Na + O_2 = 2\ Na_2O$$

Many of the oxides formed are soluble in water, and the properties of the solution will depend upon the type of element that is combined with the oxygen.

Acids are formed when the oxides of the nonmetallic elements are dissolved in water. In general, acid solutions are sour in taste; change the color of litmus, a vegetable coloring matter, to red; conduct electricity; and contain hydrogen. For example, sulfur dioxide dissolved in water produces sulfurous acid, that is,

$$SO_2 + H_2O = H_2SO_3$$

or sulfur trioxide dissolved in water forms sulfuric acid, that is,

$$SO_3 + H_2O = H_2SO_4$$

Bases are formed when the oxides of the metallic elements are dissolved in water. In general, basic or alkaline solutions feel slippery or soapy, change the color of litmus to blue, conduct electricity, and contain oxygen. They are very corrosive, and even dilute solutions will attack the epithelium of the mouth. They should not be tasted. For example, sodium oxide and water produce sodium hydroxide, that is,

$$Na_2O + H_2O = 2\ NaOH$$

Salts are formed when acids, in general, react with bases, in general, to yield substances which, in water solution, have certain properties quite different from those of either acids or bases. In fact, they are quite similar in behavior to ordinary table salt, sodium chloride. For example, sulfurous acid reacts with sodium hydroxide to form sodium sulfite, a salt used extensively in photographic developers and fixing baths, plus water, that is,

$$H_2SO_3 + 2\ NaOH = Na_2SO_3 + 2\ H_2O$$

In this example, all of the hydrogen in the sulfurous acid was displaced by sodium. This characteristic reaction of acids is called "neutralization." Under different conditions, it is possible to displace only one of the two hydrogens and form a salt called "sodium acid sulfite" and water, that is,

$$H_2SO_3 + NaOH = NaHSO_3 + H_2O$$

Similarly, it is possible to replace the hydrogen in acids with other metals to form their salts.

Another compound of interest in photography is the sodium salt of the acid called "thiosulfuric acid," which has the formula $H_2S_2O_3$. Sodium thiosulfate, $Na_2S_2O_3$, is the correct chemical name for the so-called "hypo" used in the compounding of fixing baths.

The salts discussed so far are formed from acids produced by the interaction of oxides and water. Some nonmetallic elements, the halogen group, can unite directly with hydrogen to produce strong acids. For example, the elements chlorine, bromine, and iodine form hydrochloric (HCl), hydrobromic (HBr), and hydriodic (HI) acids. When these acids are neutralized by reaction with potassium hydroxide, the halide salts – potassium chloride (KCl), potassium bromide (KBr), and potassium iodide (KI), respectively, are produced. These salts are extremely important in emulsion manufacture, because they are to form the silver halides in the emulsion.

Some of the most important acids, bases, and salts in photographic processing are included in Table II.

TABLE II

Acids	*Bases*	*Salts*
Acetic acid	Sodium hydroxide	Sodium sulfite
Hydrochloric acid	Sodium carbonate*	Sodium sulfate
Sulfuric acid	Kodalk Balanced Alkali*	Potassium bromide
	Borax*	Sodium thiosulfate
		Potassium alum
		Chrome alum

**Actually salts with strongly alkaline reaction.*

ORGANIC COMPOUNDS

The chemical substances discussed so far fall into the class known to chemists as "inorganic compounds." In general, inorganic materials contain metallic elements and are broken down by treatment at high temperatures to give an ash residue. On the other hand, organic materials are generally identified by the fact that they "burn" and often produce a residue of carbon, since they are composed chiefly of carbon, hydrogen, oxygen, nitrogen, sulfur, and sometimes phosphorus, iodine, or other elements. With the exception of carbon, these are elements which are vaporized at high temperatures.

Many of the organic compounds used in photography are not very soluble if used without some modification. They are treated chemically in such a manner that a more soluble derivative is available, usually by forming the sodium salt of the organic compound. These organic salts behave in solution in much the same way as the inorganic salts.

SOLUTIONS AND SOLUBILITY

A solution is obtained by uniformly mixing and distributing a solid or a liquid through another liquid. The substance being dissolved is called the "solute" and the liquid in which it is dissolved is called the "solvent." The extent to which the solute will dissolve in the solvent is called its "solubility," and when the solvent will hold no more of the solute, it is said to be "saturated."

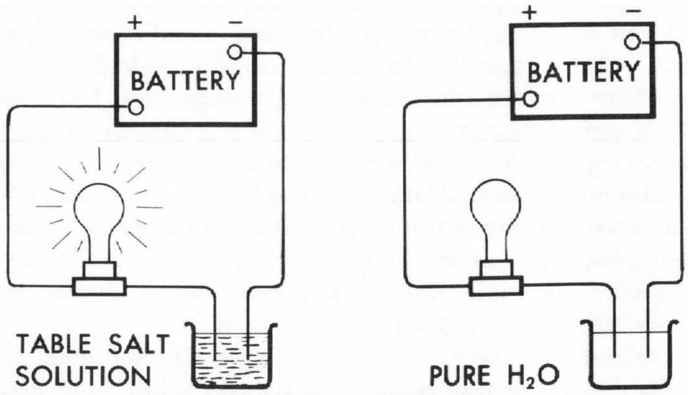
There are different kinds of solutions, classified according to the degree of solubility of the solute. A true solution is nonsettling and homogeneous to the eye. In a true solution, such as a solution of table salt, the dissolved substance is divided into single molecules or, at most, groups of a few molecules. If the mixture is less intimate and minute particles can be seen with a microscope, the mixture is known as a "suspension." A photographic emulsion is a mixture of very small particles of silver halides in a gelatin solution and is actually a suspension. A third type of solution, known as a "colloid" solution, is intermediate between a true solution and a suspension. Colloidal materials do not settle out of solution as do suspensions; at least, not nearly so rapidly. Some colloidal solutions in water have failed to settle after many years. Gelatin is a colloid and forms a colloidal solution in water. Because of this property it keeps the silver halides in a photographic emulsion uniformly dispersed and prevents them from settling out. Gelatin is known as a "protective" colloid since it protects the silver halide from settling out of solution.

The solubility of the various compounds is very important in photography. Some chemical compounds are very soluble and some are very insoluble. For example, the formation of silver halides in making photographic emulsions depends on the use of solutions of two compounds that are very soluble (silver nitrate and a potassium halide) to produce the silver halide which is extremely insoluble and therefore precipitates out of solution. Without this precipitation of a highly insoluble salt, the silver halide emulsion would never have been invented. Solubility of a compound is usually specified by the weight of chemical in grams that can be dissolved in 100 cc of water at a specified temperature. The solubilities of silver nitrate, potassium chloride, and silver chloride at room temperature are, respectively, 122, 35, and 0.0009 grams per 100 cc.

Photographic developers, fixing baths, and other solutions contain several chemicals in a single solution. These formulas are possible because of the solubility of the various chemicals even when used together in the same solution. There are, however, many chemical combinations which cannot be dissolved in a single solution because of limitations due to low solubility, reactions between some of the chemicals, or the precipitation of a reaction product.

IONIZATION

Reactions between chemicals in solution are possible because of certain properties of solutions. If some tap water is placed in a glass jar, and then two wires which are connected to an ordinary electric flashlight bulb and a dry-cell battery are placed in the water, a very weak glow might be observed. If a few teaspoons of table salt are dissolved in the water and the experiment is repeated, a much brighter light is observed. This test can be made with a whole series of chemical acids, bases, and salts, and light can be observed in each case. In other



A salt solution will conduct electricity because of the formation of ions.

words, these chemical solutions can conduct electricity. How does this happen?

If tap water is heated to the boiling point and the resulting steam is passed into a cold container, pure water minus most of the solids in it originally is obtained. The process is called "distillation," and the product is "distilled water." As the water is made more pure by repeated distillation, tests made in the conductivity apparatus will show that the current it passes becomes weaker and weaker. Practically pure water will not conduct electricity. It is concluded from these simple experiments that the salts dissolved in water are responsible for the conduction of electricity by solutions.

Certain other chemical compounds, such as sugar, when dissolved in water, do not permit an electric current to flow. Since positive and negative charges of electricity exist in an electric current, it is reasonable to conclude that table salt changes in structure to produce electrical charges in the solution, while sugar does not. The molecules of table salt (sodium chloride), when dispersed in water, tend to break up into two parts, each of which carries an equal but opposite electric charge –

$$NaCl \longrightarrow Na^+ + Cl^-$$

The electrically charged atoms of sodium and chlorine are called "ions," and their formation in water solutions is known as "ionization." The plus sign indicates that the sodium ion carries a positive charge and the minus sign indicates that the chlorine ion has a negative charge. Ionization is the process which makes possible the very rapid reactions between different chemicals dissolved in water. The ionization of chemical compounds in water solutions is extremely important in photographic processing.

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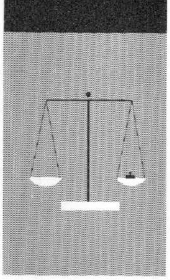


Photographic Developers

Photographic developers are special chemical solutions which react with the exposed silver halides in a photographic emulsion to make the invisible latent image visible. The latent image is composed of extremely small crystals of exposed silver halides. When these exposed crystals are acted upon by a developer, they are converted to metallic silver to form the visible image.

• Before this conversion can take place, the photographic emulsion must be properly conditioned. The gelatin in the emulsion must be softened and swelled to permit the developer to reach the exposed silver halides. The developer solution accomplishes this as well as the development of the photographic image.

CONSTITUENTS OF PHOTOGRAPHIC DEVELOPERS

The photographic developers, either packaged or mixed according to published formulas and currently used in the regular development of amateur and professional films and photographic papers, are considered here. All of these developers contain certain ingredients that perform the same functions from one formula to another, although the quantities and sometimes the individual chemicals vary.

Solvent. Water is used in mixing developers because it can penetrate and swell the gelatin of the photographic emulsion, and it can dissolve the various chemicals needed in the developer solution. In special cases, such as highly concentrated liquid developers, a small amount of a second or third solvent may be required in order to keep all of the chemicals in solution. Diethyleneglycol, similar to the antifreeze "Prestone," is often used to keep the organic chemicals in solution. Care in the choice of a second solvent is necessary because some solvents will interfere with the satisfactory development of the image.

Developing Agent. A developing agent is a chemical compound which is capable of changing the exposed grains of silver halide to metallic silver while having no appreciable effect upon the unexposed grains in the emulsion.

While some fairly simple chemical compounds can act as developing agents, the ones used in most practical developer solutions are special organic chemicals having a rather complex chemical structure. This is especially true of the color-forming developers used in color photography.

Preservative. When developing agents are dissolved in water and the solution is exposed to air, the oxygen in the air reacts with the developing agent to form highly colored oxidation products. This same reaction occurs in photographic developers when exposed to air, either while stored on the shelf or during development of the image. The preservative, usually sodium sulfite (Na_2SO_3), combines chemically with the oxidation products to prevent the formation of colored compounds and so keep the developer clear, and it also reduces the rate of the oxidation by the air. The developer solution will eventually become colored with use, but the preservative permits more exposed emulsion to be developed in the solution before this occurs.

Activator. In neutral solutions, most organic developing agents will not develop the exposed silver halides, at least to any practical extent. Certain alkalies are used in developers to make the developing agents more active. The increased activity is controlled by the choice of alkali and particularly by the degree of alkalinity it produces in a developer solution. The alkalies most generally used are borax, Kodalk Balanced Alkali, sodium carbonate, and sodium hydroxide, listed in order of increasing activity. The sodium sulfite used as a preservative is mildly alkaline, so in some special cases no additional alkali is needed.

Restrainer. Many developer formulas are available. Each is usually compounded to develop a certain type of photographic material. In most cases, a restrainer – usually potassium bromide (KBr) – is included to retard or restrain the action of the developer on the unexposed silver halides (i.e., in the nonimage areas of the negative or print). When action does occur and some metallic silver is produced in these unexposed areas, it is known as "development fog."

A typical formula for a photographic developer is:

Kodak Developer D-72	Avoirdupois— U. S. Liquid	Metric
Water, about 125F (50C)	16 ounces	500 cc
Kodak Elon Developing Agent	45 grains	3.0 grams
Kodak Sodium Sulfite, desiccated	1½ ounces	45.0 grams
Kodak Hydroquinone	175 grains	12.0 grams
Kodak Sodium Carbonate, monohydrated	2 oz 290 grains	80.0 grams
Kodak Potassium Bromide	30 grains	2.0 grams
Water to make	32 ounces	1.0 liter

Other Ingredients. There are some miscellaneous chemicals that are sometimes used in developers for special purposes. Sodium sulfate (Na_2SO_4) is added to a developer when it is to be used at a higher temperature than normal. The sulfate does not affect the development of the image appreciably, but does prevent the gelatin from swelling too much in the developer. Very high temperatures can soften the gelatin in some emulsions to the extent that they are susceptible to physical distortion, or the gelatin can even melt and the whole emulsion wash off its support.

The chemistry of photographic development is very complex, and several reactions occur simultaneously. Compounds different from those used in making up the solution are formed during development. Some developers for special purposes contain other constituents that take part in side reactions with some of the by-products from the basic development reactions.

Sometimes conventional developers are modified to formulate a so-called fine-grain developer for the purpose of forming a more uniform deposit of silver grains in the image. A chemical capable of dissolving some part of the silver halide crystals during development is added in very small quantities to the developer formula. Sodium thiocyanate ($NaCNS$) is a typical silver halide solvent and is used in formulas such as Kodak Developer DK-20.

In order to minimize the formation of fog it is sometimes necessary to use a special organic chemical whose effect will be in addition to that of the normal restrainer. Organic chemicals of this type, of which benzotriazole is an example, are known as "antifoggants." Kodak Anti Fog No. 1 and No. 2 are typical packaged antifoggants.

There are water softeners that unite chemically with the dissolved compounds, chiefly calcium and magnesium salts, which cause hardness in water. Calcium in water and in paper emulsions causes sludging in the alkaline developer solutions. Kodak Anti-Calcium added to the solution combines with the calcium and prevents the sludging.

Many proprietary or packaged developers contain minute quantities of special chemicals, but since the formulas are not published, the presence or composition of such special chemicals is not known. These are "trade secrets" incorporated in the packaged developer to give it more desirable characteristics than published or competitive formulas.

In color-forming developers, special complex organic compounds, called "couplers," are used, as discussed in Chapter VIII.

TYPES OF DEVELOPERS

Before any further discussion of developers, two distinct types should be described. They are known as "physical" developers and "chemical" or "direct" developers. They are distinguished by the method of formation of the silver in the photographic image. Actually, both types of developer produce the silver image by chemical means, but the term "physical" was applied erroneously years ago and is still used to describe this type of developer.

Physical Developers. In these developers, the silver which forms the image is *not* derived from the silver halides in the emulsion. The silver is contained in the developer solution as a soluble silver salt and during development is deposited on the latent image. Physical developers are much less efficient than chemical developers. They require much heavier exposure, and are tricky to control. While they have been useful for certain types of research on the properties of the latent image, they are not used in practical photography.

Chemical or Direct Developers. In these developers, the silver which forms the image *is* derived from the silver halides in the emulsion. This is the conventional developer used in general photographic practice. These developers "break down" the exposed silver halide, leaving metallic silver. Just how this occurs will be indicated in the next chapter.

CHEMICALS USED IN PHOTOGRAPHIC SOLUTIONS

Various types of chemical compounds, such as acids, bases, and salts were discussed in Chapter V. There are many chemicals used in the various studies and applications of the photographic process, but relatively few of these are actually used in the processing of a negative or print.

Appearance. Most of the chemicals used in preparing photographic solutions are white crystals or powders and therefore are difficult to distinguish from one another. Photographic chemicals should be kept in tightly stoppered containers which are carefully labeled. Never depend on recognition by appearance, even though some of the chemicals may be identified in this manner. Chemicals should not be left in open containers and exposed to the air, because some are attacked by the oxygen in the air and others undergo physical changes.

Solubility. The weight of material which will dissolve in a specified volume of water varies from one chemical to another. The temperature of the water has a marked effect on solubility, some chemicals being more soluble and others being less soluble as the temperature is increased. Some of the salts used in photographic solutions and their solubilities are indicated in Table III.

As stated before, the chemicals used in making developers and other processing solutions must be sufficiently soluble in water to permit all of the constituents of these baths to remain in solution in the required amounts.

TABLE III

Approximate Weights (in grams) of Chemicals Soluble in 100 cc of Water

Chemical	*Cold*	*Warm*
Sodium Sulfite	30	50
Sodium Carbonate	30	40
Potassium Bromide	70	100
Sodium Thiosulfate	200	increases
Boric Acid	5.5	17.0
Potassium Alum	14.0	50.0
Chrome Alum	25.0	40.0

The developing agents are special organic chemicals quite different in structure from the inorganic compounds listed in Table III. Many organic substances are relatively insoluble in water but can be made more soluble by forming a salt of the compound. For example, Kodak Elon Developing Agent, which is the sulfate salt of p-methylaminophenol,* is fairly readily soluble, whereas the basic p-methylaminophenol itself is only very slightly soluble. On the other hand, hydroquinone, which is a straight organic chemical, is sufficiently soluble for use directly in developers.

Water Content. A considerable number of chemicals, in their normal solid form, contain a definite proportion of water. Sodium carbonate, sodium sulfite, sodium sulfate, and sodium thiosulfate (hypo) are photographic chemicals which contain water in their crystals.

Sodium carbonate occurs in two crystalline forms with different amounts of water — $Na_2CO_3 \cdot 10\ H_2O$ and $Na_2CO_3 \cdot H_2O$.

Sodium sulfate occurs in several forms, the most complex containing 32 molecules of water.

Sodium sulfite and sodium thiosulfate each occur in one crystalline form with water — $Na_2SO_3 \cdot 7\ H_2O$ and $Na_2S_2O_3 \cdot 5H_2O$ respectively.

**This compound has also been supplied under various other trade names, including Metol, Pictol, and Rhodol.*

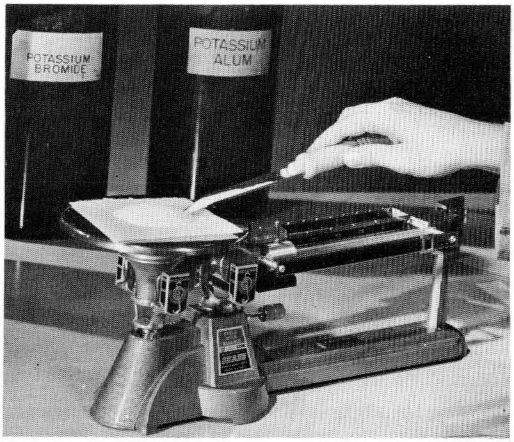
The occurrence of molecules of water in these chemicals affects the molecular weight of the compounds and, in many cases, their crystalline form. In some cases, it is possible in manufacture to remove some or all of this water of crystallization. The chemical is then called "anhydrous" if all the water is removed or "desiccated" when the water content has been reduced to a very low quantity. This means that some chemicals can be desiccated until they become anhydrous. In some instances, the chemical is more stable and has better keeping characteristics when it is desiccated. Consequently, desiccated sodium sulfite and sodium sulfate which contain practically no water, and sodium carbonate monohydrate containing one molecule of water, are generally recommended in photography. Sodium thiosulfate or hypo, however, is usually supplied as prismatic crystals which contain five molecules of water, i.e., $Na_2S_2O_3$. 5 H_2O. The anhydrous form does not keep very well and, if exposed to air, tends to absorb water. Sodium hydroxide, NaOH, also absorbs water. Chemicals which behave in this manner are called "deliquescent."

Some chemicals which contain water of crystallization do not keep well when exposed to air, because they lose water. These are said to be "efflorescent," and crystalline sodium sulfate is a good example.

Heat of Solution. When some chemicals are dissolved, heat may be either generated or absorbed from the surroundings. Considerable heat is released when sodium hydroxide is dissolved. An increase in temperature of almost 40 F occurs if 50 grams of NaOH are dissolved in 500 cc of water. This is known as an "exothermic" reaction. In these cases, cold water should always be used. If strong solutions of this hydroxide are required, an earthenware, enamelware, or stainless-steel mixing vessel should be used. If a glass mixing vessel is used, it should be placed on asbestos or cloth so that the bottom of the vessel will not stick to a varnished or other surface softened by the heat generated. Serious accidents have occurred because this precaution was not observed.

Somewhat related is the preparation of acid solutions. In order to prevent rapid and dangerous release of heat when diluting a strong acid, the acid should always be added to the water with stirring, *not* the water to the acid.

The behavior of crystalline hypo is just the opposite. A temperature decrease of 20 F is experienced when 225 grams of hypo crystals are dissolved in 500 cc of water at room temperature. This is known as an "endothermic" reaction because heat is absorbed. Warm or even fairly hot water can be used.



The recommended method of weighing chemicals. To avoid contamination, a clean piece of paper should be used for each chemical.

PREPARATION OF PHOTOGRAPHIC SOLUTIONS

The processing of photographic materials must be carefully controlled if the desired results are to be obtained. Careful mixing of the processing solutions is of major importance. Mixing vessels, trays, tanks, and darkrooms should be kept clean at all times. Chemical dust should be prevented. It is good practice to use a clean damp cloth to wipe off the work surfaces frequently, especially after weighing and mixing chemicals. Contamination can quickly spoil a developer solution. For instance, even extremely small traces of a sulfide in a developer can cause chemical fog during development.

When weighing chemicals, use scales adapted to the quantities required. Use a clean piece of paper on the scale pan for each chemical, in accordance with recommended practice, and discard the paper after each chemical is weighed.

The water supply should be examined for harmful impurities, and any present should be removed. However, it is generally not necessary to use distilled or chemically pure water. In fact, even sea water can be used to mix photographic solutions, although a sludge will likely result. This sludge is caused by the reaction of the high concentration of calcium and magnesium salts in sea water with the sodium sulfite in the developer, but it can be allowed to settle and the clear solution syphoned or drawn off. Generally, there is no appreciable effect on the development of the image.

As mentioned earlier, a photographic developer contains several chemicals, some in quite high concentration. To be certain that all of the chemicals are dissolved completely, they must be put into solution in a definite order. Developer and other processing-solution formulas are published with the chemicals listed in the order in which they are to be dissolved. *Each chemical should be dissolved completely before the next one is added to the solution.* This applies equally well to the separate parts in some packaged or proprietary photographic processing chemicals.

Most photographic solutions can be mixed at a temperature of 125 F. A volume of water equal to about half or three-quarters of the final volume of solution is measured, and the temperature is raised to 125 F. After solution of all the chemicals, sufficient cold water is added to make the final volume of solution. In mixing developers, a pinch or two of the sodium sulfite is added to the water before adding the developing agent. This helps to prevent any discoloration of the solution. Usually, any exceptions to this general procedure will be described in the mixing instructions for a specific solution.

The volume of developer solution mixed at one time should be just enough to last for two or three weeks, and the solution should be stored in tightly stoppered bottles. Some formulas must be mixed just before use because they do not keep well. Photographic developers containing sodium hydroxide (caustic soda) are examples. However, in many of these cases, the chemicals in the formula can be divided into two or more groups and dissolved in separate quantities of water to provide stock solutions that are more stable than the final developer. The working solution is easily prepared by mixing these stock solutions together, in the proper proportions, just before use.

WEIGHTS AND MEASURES

Photographic formulas are usually published in two systems of weights and measures, metric and avoirdupois. In the metric system, chemicals are weighed in fractions or multiples of grams and dissolved in cubic centimeters or liters of water. In the avoirdupois system, they are weighed in grains, ounces, and pounds and dissolved in pints, quarts, or gallons of water. With the aid of a conversion table (see Appendix), a formula given in one system can be readily converted to the other. The metric system is generally the simplest to use, since it is based on multiples of ten.

There are also two systems of temperature measurement — Centigrade and Fahrenheit. The latter is used generally in photography in this country; and the former, in European countries. The Fahrenheit scale is 32 degrees to 212 degrees from the freezing point to the boil-


Most modern processing solutions can be prepared with convenient packaged chemicals.

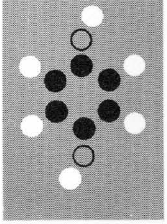
ing point of water. The difference is 180 degrees. The Centigrade scale is zero to 100 degrees from freezing to boiling point. Since the ratio of the scales is 180 to 100 or 9 to 5, a simple conversion formula is possible. To convert from Fahrenheit to Centigrade use (F—32) x 5/9 = C. To convert from Centigrade to Fahrenheit, use (C x 9/5) + 32 = F.

PACKAGED CHEMICALS

The preparation of photographic solutions has, of course, been simplified by the introduction of packaged chemicals. However, the instructions for mixing, printed on the label, should be followed carefully. The packaged formulas in dry powder form contain essentially the same chemicals as discussed above. When the mixing instructions are not followed, some of the constituents may not dissolve completely and result in turbid solutions or in sludges. Similarly, liquid preparations should be diluted correctly according to the instructions, if satisfactory results are to be expected.

In the processing of color materials, essentially the same reactions take place and the same precautions in mixing and handling solutions should be observed. However, complete color processing is more complex than black-and-white, and additional chemicals and reactions are involved because dyes must be formed to produce the color images. Also, some color processes involve reversal processing, described in Chapter XII. The different processes for color photography and the processing of color materials are described in Chapter XIII.

7



Chemistry of Development

Development is the method of making visible by using special solutions called "developers" the invisible latent image formed during exposure. How do these chemicals react in the developer in the presence of the latent image to make it visible?

• Development is actually a chemical reduction in which the exposed silver halides are reduced to metallic silver. In other words, the developer somehow causes the following reaction to take place:

$$\left.\begin{array}{l}\mathrm{Ag\,Cl}\\ \mathrm{Ag\,Br}\\ \mathrm{Ag\,I}\end{array}\right\rangle \quad \mathrm{Ag}\ \text{(metallic silver)}$$

Chemical reducers were defined years ago as substances which have an affinity for oxygen and can liberate metals from their salts. For example, if hydrogen gas is passed through a heated tube containing black copper oxide, it will combine with the oxygen to form water and leave metallic copper in the tube. This reaction, written in chemical language, illustrates the use of hydrogen as a reducing agent, and its affinity for oxygen:

$$\mathrm{CuO} + \mathrm{H_2} = \mathrm{Cu} + \mathrm{H_2O}$$

As the investigation of chemical reactions progressed, it was observed that chemical reductions occurred which did not involve hydrogen or oxygen. These reductions are the result of a change in the electrical relationships between atoms.

In Chapter V, ionization was described as the separation or splitting of a chemical in solution into positive and negative ions, e.g.,

$$\mathrm{NaCl} = \mathrm{Na^+} + \mathrm{Cl^-}$$

These ions are actually atoms of sodium and chlorine that are not neutral with respect to electric charge. According to modern atomic theory, all neutral atoms have an equal number of positive and negative electric charges. Since the sodium ion has an excess positive charge, the atom must have lost one negative charge, known as an "electron." The sodium has been oxidized. If, in some way, the excess positive charge on the sodium could be neutralized by acceptance of an electron, the sodium ion would be reduced to metallic sodium, i.e.,

$$\mathrm{Na^+} + \mathrm{e}\ \text{(electron)} \longrightarrow \mathrm{Na}\ \text{(metallic sodium)}$$

During photographic development, the emulsion is immersed in developer solution, and even though the silver halides are highly insoluble, a very small amount does dissolve and ionize to produce silver and chloride ions:

$$AgCl = Ag^+ + Cl^-$$

Since development is a chemical reduction, the reaction can be represented by the following equation:

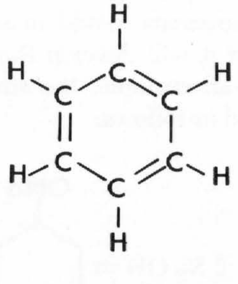
$$Ag^+ + e \longrightarrow Ag \text{ (metallic silver)}$$

Once this reaction has started, more and more of the exposed silver halides ionize and are reduced until all of the exposed halide is converted to metallic silver. However, no simple equation can be written to explain the exact chemical steps involved in development with practical developing solutions. Actually, there are several different chemical reactions occurring at the same time and the chemistry is very complex.

DEVELOPING AGENTS

These agents are special organic chemicals which have the ability, when incorporated in a developer solution, to develop the exposed silver halides without affecting the unexposed halides. They are reducing agents which provide the electrons required to reduce silver ions to metallic silver.

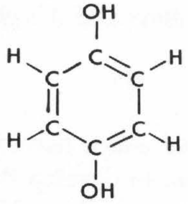
The most commonly used developing agents are all related chemically to benzene, which has the formula C_6H_6. Organic chemicals are usually represented by *structural* formulas which indicate the relative positions in space of the atoms in the molecule. Benzene is represented by the following structural formula:



which shows that there are six carbon atoms in a ring, with one hydrogen atom attached to each carbon atom. Since this particular arrangement of six carbon atoms forms a basic unit or building block in a very large number of compounds, it is generally represented by the simplified symbol:

Each of the angles of this hexagon represents one of the six carbon atoms and its attached hydrogen atom.

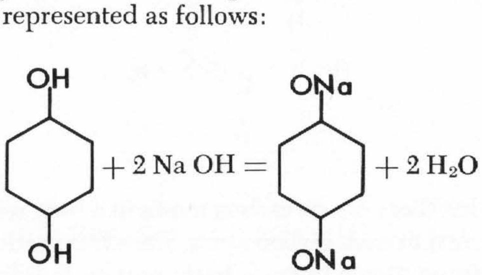
By chemical reactions, small or large groups of atoms can be substituted for one or more of the hydrogen atoms. Thus, hydroquinone has the structure:



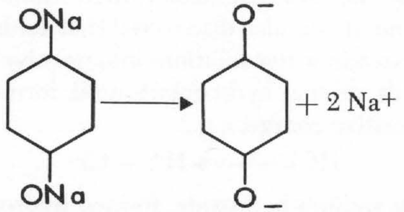
or

In reading the simplified symbol, it is understood that the two OH groups have replaced two of the hydrogen atoms, but that the other four hydrogen atoms are still in place at the four plain angles. The OH groups which have replaced two of the six hydrogens are called "hydroxyl" groups. Other commonly used developing agents are Kodak Elon Developing Agent, para-aminophenol, and paraphenylenediamine.

Generally, organic developing agents will not develop a silver image by themselves. It is necessary to add an activator to condition the developing agent so that it will develop the exposed silver halides. Using hydroquinone as an example, the effect of the activator, an alkali, can be represented as follows:



The sodium hydroxide reacts with the hydroquinone to form the sodium salt of the developing agent. This salt, being in a water solution, ionizes or dissociates in the same manner as sodium chloride or table salt –



The negative ion has two excess negative electric charges or electrons. It can give up these electrons to the silver ions formed from the silver halide, and this allows the reaction,

$$Ag^+ + e \longrightarrow Ag$$

or the reduction of the silver ions to metallic silver. *It must be remembered that this represents the end result of several chemical reactions.* However, it provides some idea of how the silver image is formed in the developer.

ACTIVATORS

The following alkalies are most commonly used as activators in photographic developers:

Sodium hydroxide, $NaOH$
Sodium carbonate, Na_2CO_3
Kodalk Balanced Alkali
Borax

These are listed in the order of decreasing activity, which means that developers containing sodium hydroxide are much more active than those containing borax. A given amount of image silver will be formed in much less time in the highly active developers than in the low-activity developers.

The activity of a developer is controlled, to a large extent, by the alkalinity of the solution, which depends on the particular alkali and the quantity of it used. The relative alkalinities of developers are generally indicated by pH values. The pH of a developer solution is affected by several of the chemicals used in the solution, but is determined primarily by the characteristics of the alkali employed. What is meant by the pH of a solution ?

pH

Two interesting developments in the early days of chemistry led to the introduction of the pH concept. Acids and bases (or alkalies) were first recognized by the fact that acids turned litmus paper* red and bases turned it blue. It was also discovered that acids, bases, and salts ionized or dissociated in water solutions into positively and negatively charged ions. Acids, such as hydrochloric acid, formed hydrogen ions having a single positive charge, e.g.,

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

and bases, such as sodium hydroxide, formed hydroxyl ions having a single negative charge, e.g.,

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

It was concluded that the changes in the color of litmus paper were produced by the hydrogen or hydroxyl ions present in the solution. While litmus paper can show whether there are more or less hydrogen ions than hydroxyl ions present it soon became evident that a method was needed for determining the quantity or concentration of the hydrogen or hydroxyl ions present.

Ordinary water can be written chemically as HOH. It contains both hydrogen ion and the hydroxyl ion in equal concentrations:

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

But water does not ionize as readily as acids, bases, and salts. In fact, the electrical conductivity of pure water is so very low that it indicates that the degree of dissociation or ionization is so small that ordinarily it might be considered negligible. The fact that water does ionize slightly, however, can be used as a basis for the determination of acidity or alkalinity in water solutions. This can be done by using a relationship discovered between the concentrations of hydrogen and hydroxyl ions. The product obtained by multiplying together the numerical values of the two concentrations is a constant which can be expressed as follows:

$$[H^+] \times [OH^-] = K$$

This means that the product of the concentrations is always the same in any water solution, and that the concentration of one ion can be calculated from this relationship when the concentration of the other ion has been determined by analysis. For instance, in pure water the concentrations of hydrogen and hydroxyl ions are equal and are

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**Litmus paper is an absorbent paper impregnated with a special organic compound capable of changing color in acid and basic solutions.*

0.0000001 when expressed in gram mols per liter. Thus, the value of K is

$$0.0000001 \text{ x } 0.0000001 = 0.00000000000001$$

In a solution of a weak acid, if the hydrogen-ion concentration is 0.00001, the hydroxyl-ion concentration would be 0.000000001; while, with a moderately strong alkali, if the hydroxyl-ion concentration is 0.0001, the hydrogen-ion concentration will be 0.0000000001. In all cases, the product of the two concentrations is 0.00000000000001. This is called the "dissociation constant of water."

It is apparent that it is difficult to write, or read, numbers like these, but very often they are written for convenience as factors of appropriate powers of 10. Consider the numbers in the following table and their simplified expression in exponential form:

$$\begin{aligned}
100 &= 1.0 \text{ x } 10^{2} \\
10 &= 1.0 \text{ x } 10^{1} \\
1 &= 1.0 \\
0.1 &= 1.0 \text{ x } 10^{-1} \\
.01 &= 1.0 \text{ x } 10^{-2} \\
.001 &= 1.0 \text{ x } 10^{-3} \\
.0001 &= 1.0 \text{ x } 10^{-4} \\
.00001 &= 1.0 \text{ x } 10^{-5} \\
.000001 &= 1.0 \text{ x } 10^{-6} \\
.0000001 &= 1.0 \text{ x } 10^{-7}
\end{aligned}$$

Thus, the value of K stated as 0.00000000000001 can be written as $1.0 \text{ x } 10^{-14}$, and the relationship between the hydrogen- and hydroxyl-ions in pure water as

$$[H^{+}] \text{ x } [OH^{-}] = K = 1.0 \text{ x } 10^{-14}$$

It can be assumed that pure water is neutral, and therefore that all neutral solutions will have the same hydrogen-ion concentration as pure water, or $1.0 \text{ x } 10^{-7}$.

In an acid solution there will be a higher concentration of hydrogen-ion than of hydroxyl-ion, and in a very strongly acid solution the actual value may approach $1.0 \text{ x } 10^{-1}$. On the other hand, in an alkaline solution the hydrogen-ion concentration decreases with respect to its concentration in pure water and approaches the value $1.0 \text{ x } 10^{-14}$ as the solution becomes extremely alkaline. A decrease in the concentration of hydrogen-ions can be used to express an increase in hydroxyl-ions.

In practice, it has been found most satisfactory to determine the concentration of the hydrogen-ion, whether the solution is acid, neutral, or alkaline. But it was necessary to simplify the method of expressing the hydrogen-ion concentration before it was widely accepted. Sorenson made the first simplification by suggesting that the exponents only be used, without their negative sign, e.g., $1.0 \text{ x } 10^{-14}$ could be written as 14, and he called these figures "pH values." As a result, the following pH scale came into being.

pH

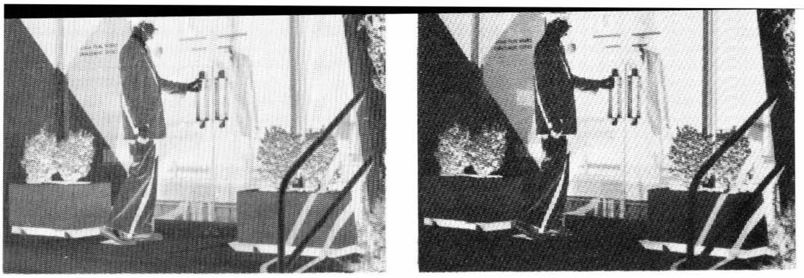
$$\left.\begin{array}{r}14\\13\\12\\11\\10\\9\\8\end{array}\right\}\text{alkalinity}$$

$$7\;\}\;\text{neutral}$$

$$\left.\begin{array}{r}6\\5\\4\\3\\2\\1\end{array}\right\}\text{acidity}$$

With suitable equipment, such as pH meters, this scale permits the determination of the number of times the acidity or alkalinity exceeds that of pure water. Since the pH scale consists of the exponents in the expression of hydrogen-ion concentration, the actual hydrogen-ion concentrations represented by successive numbers in the scale are related to each other by a factor of 10. For example, in the acid range, the concentration of acid increases as the pH value becomes smaller. A solution at $pH = 5.0$ contains 10 times more free hydrogen-ion than one at $pH = 6.0$, while a solution at pH 4.0 contains 100 times more than one at pH 6.0. Similarly, a solution at pH 10.0 contains 100 times more hydroxyl ion than one at pH 8.0, and so on.

As stated before, the alkali used in a developer controls its activity or the rate at which it develops the silver image. This effect is related primarily to the pH value produced in the developer solution. Developers with sodium hydroxide have a pH of approximately 12.0, and are extremely active; those with sodium carbonate have a pH of about 10.2 and are quite active; those with Kodalk Balanced Alkali have a pH of about 9.8 to 10 and have medium activity; and those



These negatives, exposed identically, were developed for the same times in Kodak Developer D-76 with normal pH of 8.6 (left) and pH adjusted to 9.5 (right). Note the increase in density and contrast produced by the more active developer.

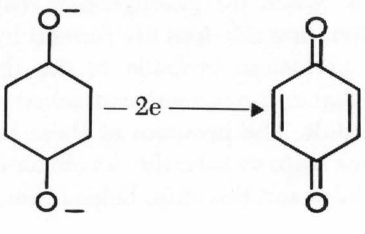
with borax have a pH of about 8.5 to 9.0, with correspondingly low activity and long development time.

Many materials that are ionized in solution exert a "buffer action," which means that they tend to resist or retard any change in the pH value of the solution. Thus, considerable quantities of acid or alkali can be added to a buffered solution, or the solution can be diluted, with only a very gradual change in pH value. The alkalies used in photographic developers are selected to provide buffering action at the desired pH levels. It is important that the developer maintain its characteristics while a considerable quantity of exposed photographic emulsion is processed in it; otherwise, the developer would not be very practical to use.

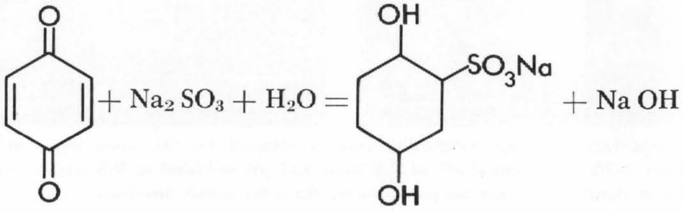
PRESERVATIVE

If a developing agent is dissolved in water, the solution will turn brown because of the breakdown of the developing agent by the action of the air (oxidation). When alkali is added to the solution, the breakdown takes place much more rapidly. Therefore, a preservative, usually sodium sulfite, is added to developer solutions to prevent this oxidation and thereby keep the solutions clear.

The sodium sulfite reacts with the oxidation products of the developing agent as fast as they are formed. Using the same example as on page 47, hydroquinone, the reactions may be written as follows. When the electrons of the negatively charged developing-agent ion are removed, quinone is formed:



Quinone reacts with sodium sulfite in the presence of water to form colorless sodium hydroquinone sulfonate and sodium hydroxide:



This is a very simplified representation of what actually happens, because other organic chemicals may be formed during oxidation of the developing agent and different ones are formed with the various developing agents. Generally, the sulfite salts formed play no part in the development, but there are some which are themselves developing agents and therefore contribute to the subsequent development.

The preservative action of the sulfite is its ability to prevent the developing agent in alkaline solution from being attacked by the oxygen in the air. If quinone, for example, were allowed to form in the developer solution, it would speed up the oxidation reaction. A chemical which speeds up reactions is known as a "catalyst." The sulfite prevents the accumulation of such a catalyst.

RESTRAINER

Potassium bromide is commonly used in development to restrain the formation of chemical fog, which is silver produced by action of the developer on unexposed silver halide. The bromide also assists in producing more uniform development. Although the addition of potassium bromide to a photographic developer may affect the rate of development of the image, it usually depresses the rate of fog formation to a greater degree than the rate of development. As a result, more efficient development is obtained. The chemical action of potassium bromide is quite complex and cannot be fully explained without considering in detail the proposed theories of photographic development. However, the general course of the action seems to be somewhat as follows. When the photographic material is placed in the developer solution, bromide ions are formed by the ionization or dissociation of the potassium bromide in the developer solution. These ions adsorb—that is, are somehow attached—to the surfaces of the silver halide crystals. The presence of these bromide ions (Br^-) on the crystal surfaces helps to keep the developer from attacking the unexposed silver halides and therefore helps to retard fog formation.

8

Chemistry of Color Development

In the development reaction, when the exposed silver halide is reduced to metallic silver, the developing agent is oxidized. The compounds formed by this oxidation are quite reactive and can be used to form color images.

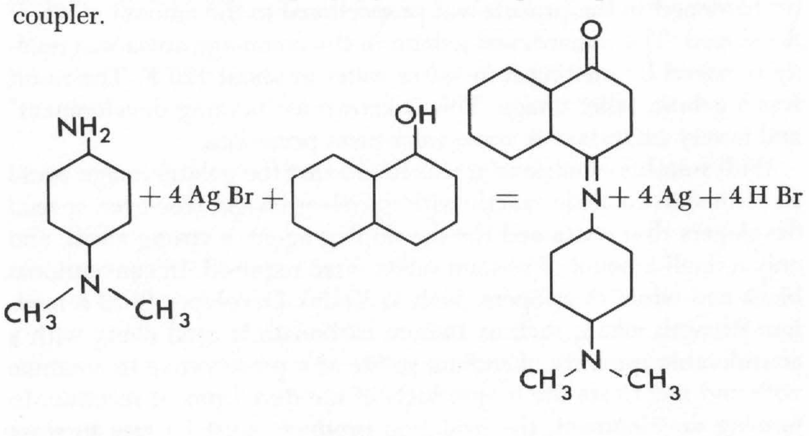
• It was observed as early as 1879 that some photographic developing agents produced a hardened gelatin image during the development of the silver image in a photographic emulsion. The gelatin image coincided with the developed silver image, and the thickness of gelatin hardened in the process was proportional to the amount of silver developed. The unhardened gelatin in the nonimage areas was readily removed by melting it in warm water at about 120 F. The result was a gelatin relief image. This is known as "tanning development" and is very important in some color-print processes.

With suitable emulsions, it was found that the gelatin image could be formed to coincide exactly with the silver image. However, special developers that contained the developing agent, a strong alkali, and only a small amount of sodium sulfite were required. In conventional black-and-white developers, such as Kodak Developer D-72 a medium-strength alkali, such as sodium carbonate is used along with a considerable quantity of sodium sulfite as a preservative to combine with and inactivate the by-products of the development reaction. In tanning development, the oxidation products must be free to react with and harden the gelatin, and the sulfite therefore must be left out or used in very small quantity. A very strong alkali, such as sodium hydroxide, is used to provide solutions of high pH to accelerate the oxidation of the developing agent and increase the hardening action. The gelatin relief image produced can absorb dye from a bath in proportion to the thickness of gelatin present, and the absorbed dye can be transferred to special receiving materials by bringing the dyed relief into close contact with the receiving surface. This is the basis of the Kodak Dye Transfer Process for making color prints on paper.

COLOR DEVELOPERS

The oxidation by-products of the basic development reaction can be used in various ways. For instance, under suitable conditions they can combine with certain other organic compounds to form colored dyes.

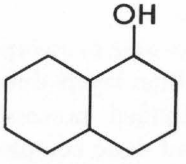
The dyes are formed as the result of a coupling reaction between the developer oxidation products and special dye formers, called "couplers," added to the system. Fortunately for the simplification of practical color processes, one developing agent can be used with different couplers to form dyes of the various colors needed. The color of the dye that is formed during color development is dependent on the chemical structure of the coupler. It is sufficient in this discussion to state that part of the coupler molecule is the color-forming part which determines the color of the dye formed, while the remaining part of the molecule affects the solubility of the coupler and its ability to diffuse or penetrate the emulsion layer. Both the coupler and the developer affect the solubility and the stability of the dye formed. The reaction is illustrated below with dimethyl-para-phenylenediamine as the developing agent and alpha-naphthol as a blue coupler.



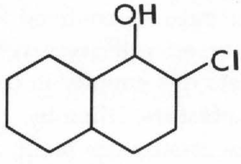
dimethyl-para-phenylenediamine **alpha-naphthol** **indo-phenol blue**

SELECTION OF COUPLERS

In any group of dye couplers, such as those producing blue or cyan dyes, small changes in the structure of a coupler molecule can cause a change in the color. For example, if chlorine is added to the alpha-naphthol coupler molecule, a different shade of blue dye is formed when it reacts with the oxidation by-product of the developing agent. The formulas for the two couplers are:



and



alpha-naphthol

chloro-alpha naphthol

Dye solutions absorb different wavelengths of light according to the color of the dye, and measurements of this absorption show the differences in the colors of dyes. The dye images formed in a color film with the two couplers alpha-naphthol and chloro-alpha-naphthol have their maximum absorptions at wavelengths of 630 mμ and 654 mμ, respectively. By proper choice of the coupler, it is theoretically possible to produce any desired color. This is important in color photography because it makes possible the selection of the best combination of yellow, magenta, and cyan dyes to produce good color pictures.

In color development, silver is formed (in a given emulsion) in proportion to the exposure of the silver halides, and simultaneously the oxidation product of the developing agent reacts with the dye coupler to give a color image proportional to the silver image. Therefore, during color development there is formed an image which consists of silver and dye produced in proportion to the original exposure.

The requirements for a practical color-development system include: formation of an insoluble dye that will remain in the film; the choice of couplers to produce the proper color; dyes with good stability against fading; and developing agents that are not excessively toxic. Research has provided compounds that satisfy these requirements quite well for all practical purposes. There are two general types of color-development processes distinguished by the method of using the dye couplers, namely: (a) those which require the use of couplers in the color-developer solutions and (b) those which have the dye couplers incorporated in the emulsion layers.

The first commercially successful three-color dye-coupling reversal process was the Kodachrome Process. It consists essentially of three separate emulsion layers containing silver halides, with each layer sensitized differently to respond in exposure to specific parts of the visible spectrum. Each of the three complementary dyes — yellow, magenta, and cyan – is formed in its respective layer in three successive color developers containing appropriate developing agents and couplers. This means that the chemical reactions in each color developer must be confined to a single layer.

However, scientific research has made it possible to incorporate the appropriate dye coupler in each of the emulsion layers during product manufacture, thereby permitting simplified processing. The coupler molecules are made much larger and more complex so that they cannot wander away from their location in the emulsion layer, but their ability to react with oxidation by-products of the developing agent is not impaired. Kodak Ektachrome Film is a color product of this type. The number of processing steps is reduced because only one color developer is required. The developer reacts with the dye coupler in each emulsion layer in proportion to the silver image formed in that layer. This simplification of the color process has made it possible for the individual photographer or commercial laboratory to process color films.

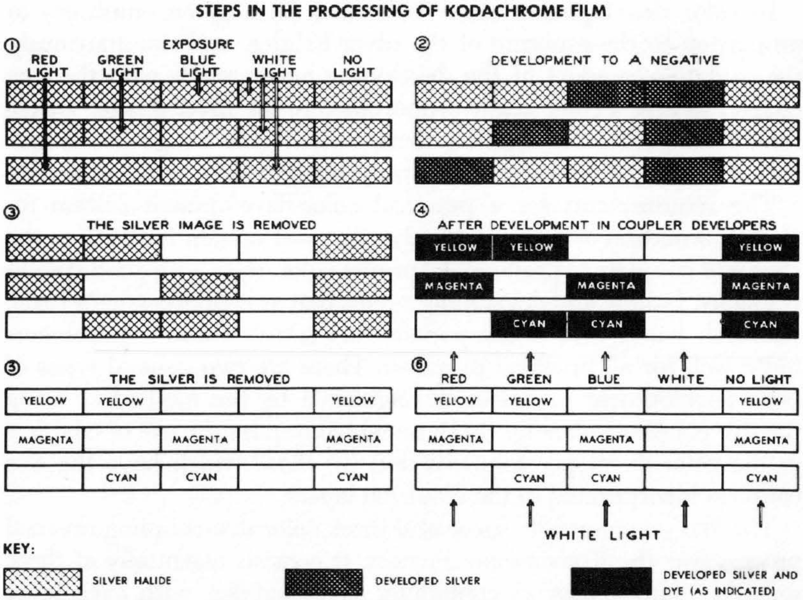


FIGURE 5 The Kodachrome process

COMPOSITION OF COLOR DEVELOPERS

In general, color-forming developers are quite similar in composition to the conventional black-and-white developers in that they contain the same basic ingredients of developing agent, activator, preservative, and restrainer. However, the proportions of the various ingredients are quite different, and some of the ingredients, such as the color-developing agent, are much more complicated compounds. Also, the color developer usually contains additional special ingredients, even when the dye coupler is incorporated in the emulsion.

This can be illustrated by comparing the typical black-and-white developer formula on page 36 (Kodak Developer D-72) and the following typical color developer which is used with couplers incorporated in the emulsions.

Color Developer (Kodak SD-35)

Water, 70 to 80F (21 to 27C)	1.0 liter
Benzyl Alcohol	6.0 cc
Stir about 5 minutes to insure complete solution.	
Sodium Hexametaphosphate or Calgon	2.0 grams
Kodak Sodium Sulfite, desiccated	5.0 grams
Trisodium Phosphate · $12H_2O$	40.0 grams
Kodak Potassium Bromide	0.25 gram
0.1% solution of Kodak Potassium Iodide	10.0 cc
Kodak Sodium Hydroxide	6.5 grams
Kodak Color Developing Agent, CD-3 4-amino-N-ethyl-N-(β-methane-sulfonamidoethyl)-m-toluidine sesquisulfate monohydrate	11.33 grams
Ethylenediamine Sulfate	7.8 grams
Citrazinic Acid (2,6-Dihydroxy-isonicotinic acid)	1.5 grams

Developing Agent. Special developing agents are required for color processing to produce oxidation products that react with the incorporated couplers to form the dye images.

Frequently, they require a "booster" in addition to the alkali activators in the formula, and benzyl alcohol is added for this purpose. It is an organic solvent and, as such, probably accelerates the penetration of the developing agent into the different layers of the color material. The concentration must be carefully controlled because too much or too little benzyl alcohol can affect the sensitometric characteristics of the image. Some of the silver halide solvent, ethylenediamine sulfate, is also used.

Activator. For this purpose two alkalies are used, trisodium phosphate and sodium hydroxide. These are stronger alkalies than sodium carbonate and are used both to provide a higher pH for this developer and to buffer the solution to increase its capacity to neutralize acid by-products of the development reaction, as well as to insure the solubility of the developing agent.

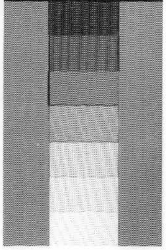
Preservative. Although the same preservative, sodium sulfite, is used, the concentration is very much lower than in the black-and-white developers. In color development, the oxidation products of the developing agent must be free to react with the coupler for dye formation. A high concentration of sulfite would prevent this. On the other hand, some preservative is required to minimize aerial oxidation and to react with the unused oxidation by-products and prevent stains in the processed film.

Restrainer. Potassium bromide is used, but in considerably lower concentration and in combination with potassium iodide in the correct proportion.

Auxiliary Coupler. It is difficult in most color processes to obtain good control over contrast. Adjustments in the concentration of other constituents, such as activator, developing agent, etc, usually affect emulsion speed. However, a special compound like citrazinic acid can be added to the color developer to react with some of the oxidation products of the developing agent to form colorless compounds. This mechanism makes it possible to control the relation between the amounts of silver and of dye formed in the image, and thus control the contrast of the color image.

9

The Measurement of Development



Up to this point photographic developers have been considered with respect to the action of the developer, the composition of developers, the mixing of developers, and the chemistry of development. In the practical use of developers, measurement of the degree of development is important. It is therefore discussed here.

• In order to understand clearly the effects of various factors in development, some means of measuring the image silver formed during development is required. The measurement of development effects is a part of "sensitometry." As early as 1890, Hurter and Driffield studied the relationship between the exposure and the amount of silver formed during development.

Light was passed through the silver image, and a measurement of the fraction of the light getting through was used as an indication of the amount of silver formed in the image. This fraction usually expressed in percent, is known as the "transmission." However, the transmission decreases as the image blackness, or amount of silver, increases. It would be more descriptive to use the "opacity," which is the inverse of the transmission, and thus increases with increasing silver.

Hurter and Driffield found that, for a number of reasons, it is more meaningful to use the logarithm of the opacity, or "density," instead of the arithmetic value of opacity. For one thing, the human eye judges tone differences, or brightness differences, in logarithmic terms. For another, because of the way in which an image absorbs or stops the light, it was found that, for any given emulsion type, the amount of silver in the image is almost directly proportional to the density.

Mathematically, these relations can be expressed as follows:

$$\text{Transmission (T)} \quad \frac{\text{light striking the image}}{\text{light passing through the image}},$$

$$\text{Opacity (O)} = \frac{1}{\text{Transmission}} = \frac{\text{light striking the image}}{\text{light passing through the image}}, \text{ and}$$

Density = logarithm of opacity = log O.

The image is, of course, the result of the development of exposed silver halides. The exposure (E) is the product of the light intensity (I) and the time of action of the light (t), i.e.,

$$E = I \times t$$

Interpreting this with respect to the use of cameras, the intensity is controlled by the brightness of the subject and by the lens aperture; and the time, by the shutter speed. Exposure is usually expressed in logarithmic terms as log exposure or log E. This is not only convenient in plotting graphs, because both the density and exposure scales are expressed in a similar manner, but it is justified by a number of other theoretical as well as practical considerations.

Hurter and Driffield plotted the D and log E values on graph paper and obtained a curve, called either the "H & D curve" or the "characteristic curve" (Figure 6), which is characteristic of sensitized materials. This simple S-shaped curve shows the relationship between increasing exposure and the increased density formed under the conditions of development.

There are some terms used in photography to describe information obtained from the characteristic curve that should be familiar to the reader. There are three parts to the curve. These are known, respectively, as the "toe," that portion between A and B in Figure 6; the "shoulder" between C and D; and the "straight-line portion," between B and C. The slope, or gradient, is highest in the straight-line portion of the curve, and the gradient decreases in both the toe and shoulder.

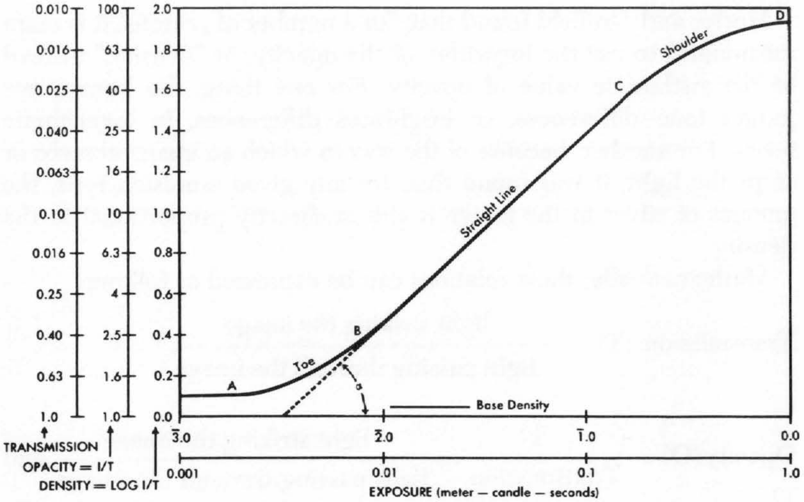


FIGURE 6 The characteristic curve

The slope of the straight-line portion indicates the development contrast of the negative or print material represented by the characteristic curve, while the changing slopes of the toe and shoulder indicate the amount of compression of the tones likely to be encountered in the shadow and highlight areas. The more gradual the change of slope, the greater the range of tones that can be reproduced.

The slope of the straight-line portion, known as "gamma," can be measured easily. It is a function of the angle (a) between the log E axis of the graph and the straight-line portion of the curve (Figure 6). Gamma, therefore, provides a convenient means for measuring or describing the degree of development of the image. It is one of the important factors involved in the contrast of the image.

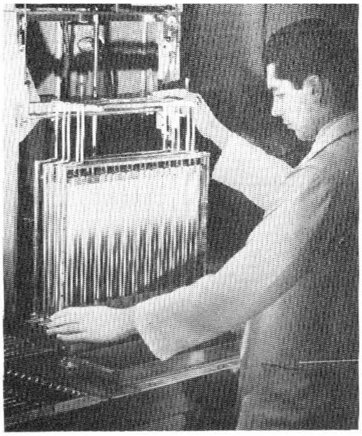
SENSITOMETRY

The work of Hurter and Driffield is now the basis for the testing of photographic materials both during and after manufacture, for the control of processing, and so on.

In order to be useful and practical, it must be possible to reproduce quite accurately from time to time the characteristic curve for any product. This requires the use of a standard test object and special equipment to provide reproducible exposure, development, fixation, and washing, or, in other words, reproducible exposure and processing. In addition, equipment is required to measure the densities in the processed photographic materials. These requirements have been satisfied during recent years, a fact which has made possible "sensitometric testing."

Test Object. This is usually a "step tablet" which consists of a series of densities, the density of each successive step being a certain amount greater than the density of the preceding step. There are many kinds of step tablets for this purpose, but probably the most commonly used one, shown on page 62, consists of 21 steps ranging in density from zero to 3.0, with each step increasing by a density difference of 0.15.

Sensitometer. This is a carefully calibrated exposing device in which the exposing lamp is operated under such conditions that the light output or intensity is reproducible from one test to another. The step tablet or other test object is accurately located with respect to the light source, thereby permitting the illumination of the test sample to be reproduced exactly in every test. By appropriate means, the unit is calibrated or adjusted before each exposure, if required. The mechanical parts are designed so that the exposure of a plate, film, or paper product can always be duplicated.

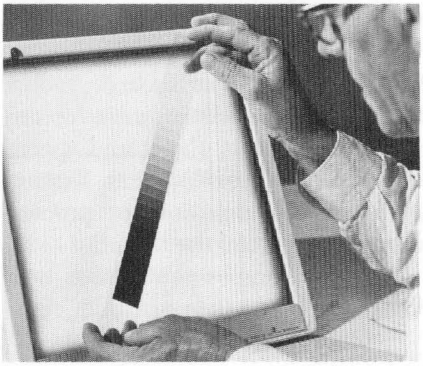


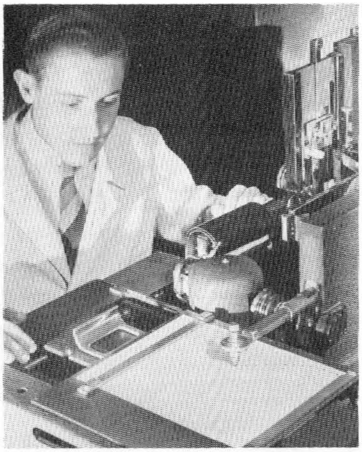
Above — Test samples of the material are exposed in a sensitometer like this one.

Above right — The sample receives uniform mechanical agitation during processing.

Below — The processed test sample.

Below right — A recording densitometer measures and plots the densities of the test sample.





Sensitometric testing of photographic materials during manufacture.

Processing. This cycle of operations, particularly the development, must also be accurately duplicated. It is important to control the composition of the processing solutions, the time, the temperature, and the amount of agitation. For the routine testing of sensitized materials the developers and fixing baths are mixed in large volumes so that the same solutions are available over considerable periods of time. It is not unusual in very extensive sensitometric testing operations to mix and store processing solutions in 500-gallon volumes. The storage tanks are usually located at a level above the testing stations to permit gravity flow as required.

Since temperature of the solution is difficult to adjust and duplicate just before each test, it is customary to keep the storage tanks submerged in a water bath adjusted to 68 F, the processing temperature considered as standard by the American Standards Association, Inc. Similarly, the processing tanks are also submerged in water baths kept at 68 F.

Agitation is probably the most difficult factor to control. The oxidation products of the developing agent and the alkali halides which are formed during the development reaction can interfere with development. Generally, when no agitation is employed, these by-products accumulate at the emulsion surface and within the emulsion, thereby slowing down the development. Agitation should therefore be uniform and sufficiently vigorous to remove the by-products of development and allow fresh developer to reach the emulsion continuously throughout the development time. Efficient agitation is also required in the rinse bath, in the fixing bath, and during washing.

Therefore, special agitation devices have been designed to accomplish this difficult operation. One system used at the present time for processing sensitometric tests consists of moving vertical blades placed approximately at right angles very close to the emulsion surface. The blades and test samples are immersed completely in the solution and the blades are moved automatically from side to side. In effect, the blades "wipe" the emulsion surface, causing the partially used developer to be brushed away from the surface and fresh developer to flow into contact with the surface. The speed of this operation is adjusted to provide uniform development.

Densitometer. This is an optical instrument designed to measure accurately the optical density of the developed photographic image. In routine sensitometry, it is used primarily for measuring the densities of the reproductions of the standard step tablet. In practical photography, it can be used to read the densities in negatives in those applications where accurate control of processing is required.

VALUE OF SENSITOMETRY

For many years the importance of controlled exposure and processing was realized. However, it was difficult to determine accurately the true effects of all the factors involved. The development of the techniques described above made this possible. For example, under these controlled test conditions, one factor, such as the emulsion, can be changed, and since all of the other factors are controlled and reproducible, the characteristics of the new emulsion can be compared to those of any other emulsion processed under the same conditions. Similarly, the effects of temperature, agitation, developer composition, etc, can be studied individually so long as all of the other factors are maintained under standard conditions.

One or two examples will indicate the value of the sensitometric control of photographic processing. The first example concerns the motion-picture industry, where hundreds of thousands of feet of 35mm film must be processed to have exactly the same photographic characteristics throughout the entire length. This is accomplished within very close limits by carefully controlling the developer composition, temperature, agitation, time of development, and so on. Standard step tablet exposures are processed by developing them along with the exposed film, as a check on the processing conditions which were originally established by this technique. The result of this carefully controlled processing is the high-quality motion picture presented to the public. Just imagine the results from film to film or even within the length of a single film if careful processing were ignored.

Obviously, it is impossible for everybody involved in photographic processing to own such elaborate equipment as indicated above. But there are many cases in which some idea – even though rough – of the duplication of processing conditions is helpful. Very simple equipment is adequate. It is necessary to include only regular processing trays, a tray thermometer, and a step tablet. Different sizes of step tablets, with or without a calibration curve, can be obtained from photographic manufacturers. Film or paper is exposed by passing light through the step tablet for a time just sufficient to reproduce most of the tablet on subsequent development. The developer tray is usually set in another tray or sink of water adjusted to the processing temperature, preferably 68 F. The same agitation technique should be employed each time a test or final negative or print is processed.

It is not possible to outline here all of the very useful applications of these methods, but it is important to know that processing can be controlled to any degree of accuracy, dependent upon the particular application and the availability of suitable equipment.

Sensitometric control of processing does not necessarily involve the use of special sensitometers and densitometers. A great majority of people using photographic materials refer to the exposure and processing recommendations given on the instruction sheets which usually accompany the packaged film or paper. These recommendations are the result of carefully controlled tests made by the manufacturers on their products. Therefore, in a sense, each time that printed instructions for a specific product are followed by the photographer, he is using sensitometry. Data books also contain information about the handling of photographic products, and these data are the result of controlled tests. Data books and instruction sheets provide the best guide available for the correct handling of a manufacturer's product. *It is not a safe practice to use the processing recommendations given for one product in the processing of another product for which the instructions were not intended.*

COLOR SENSITOMETRY

If sensitometric testing is of value in black-and-white photography, it is indispensable in color photography. This is because, for correct color reproduction, at least three different color images must be properly balanced for density, contrast, and tone-reproduction curve shape, and sensitometric tests provide the information which makes this possible.

In the case of color processes which make use of color-separation negatives, such as the Kodak Dye Transfer Process, the sensitometric procedures are essentially the same as for black-and-white. The chief difference is that a separate curve is obtained for each of the primary color images, and these curves must have the proper relationships to each other, as required by the characteristics of the process.

Sensitometric tests are considerably more complicated in the case of color processes, such as Kodachrome and Kodacolor, in which the three color images are formed in three superimposed emulsion layers that cannot be separated. Not only must the exposing light be adjusted to a known and reproducible intensity, but also its color quality must be carefully adjusted to suit the characteristics of the color material being exposed. Then, after processing, the density of each of the three different color images must be measured with light of the appropriate color.

Full sensitometric testing, such as is required in the manufacture of color-photographic materials, is very complicated, both in the procedures and in the interpretation of the results. Fortunately, much less complicated procedures can be used for the checking and control of color processing. For instance, the Eastman Kodak Company supplies specially exposed strips of Kodak Ektachrome and Kodacolor films, to allow quality control in the processing. One of these strips is processed along with each batch of films. Some information can be obtained from a visual examination of the exposed strip, and the full numerical information needed for a check on the processing can be obtained from a few simple density measurements.

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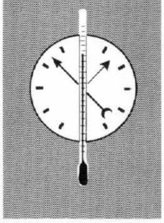


Control of Development

There are important factors in the practical use of developers which affect the degree of development produced. These must be properly controlled in order to produce negatives and prints of good quality.

• Development is the most important operation in the photographic process because it forms the image, and the degree of development controls the density and gradation of the image.

In the earlier days of photography, all photographic materials were developed by inspection. Then, the sensitivity to light of even the negative materials was low enough to permit the photographer to watch the image develop under a safelight. With experience, excellent results were obtained, and a skilled photographer often could produce a series of negatives having almost the same characteristics. However, the need for faster emulsions resulted in high-speed orthochromatic and panchromatic emulsions which could not be developed by inspection under a safelight. Fortunately, sensitometry provided the means for controlling development of these materials in total or near-total darkness. Thus, the instruction sheet tells the photographer to develop a film in a specified developer for so many minutes at a certain temperature and with a certain degree of agitation.

When any part of the specified procedure is disregarded or changed, the results will likely be different than expected. Assuming that the exposure is correct, there are several factors related to development that should be kept under control.

PHYSICAL FACTORS

Some of these factors are concerned with the physical conditions involved in development and include the effect of the time of development, the temperature, and the agitation of the developer. These effects can be illustrated by indicating the changes in the characteristic or H and D curves. In the following discussion it is assumed that processing is controlled by the best sensitometric methods so that all factors are kept uniform except the single one under consideration. Since these factors are fundamental in the processing of all emulsions, an H and D curve for a typical emulsion, X, is used.

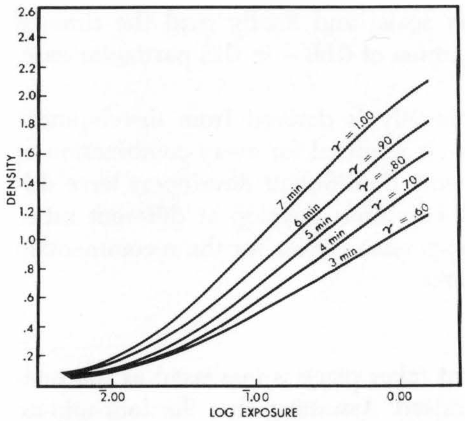


FIGURE 7 Effect of increasing development times

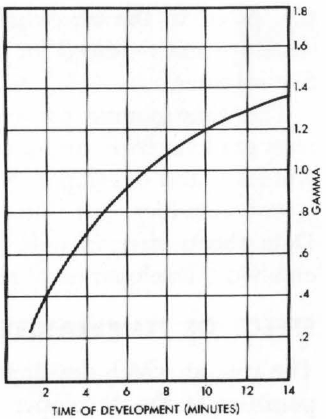


FIGURE 8 Time-gamma curve

TIME OF DEVELOPMENT

For most emulsions, a certain length of time in the developer is required. This is known as the "induction period," that is, the time required to condition the emulsion and start the chemistry of development. After development has started and as the time is increased, more image silver is formed, and the density increases in some proportion to the original exposure. The curves in Figure 7 illustrate the effect of increasing times of development.

It is apparent that the gamma, or the slope of the straight-line portion of the curve, increases as the time of development is increased. Just which curve indicates the best time of development will depend upon the particular emulsion in use and the purpose for which it is being used. In any case, it is generally true that the time of development can be varied over a limited range to obtain a desired gamma.

The times of development in a family of curves like this can be plotted against the measured gamma values to produce a very practical and valuable curve called the "time-gamma" curve. These curves have the general appearance of the one shown in Figure 8.

From this type of curve, it is possible to determine the time of development needed to obtain a definite gamma or to tell what gamma will be obtained for a certain time of development at 68 F. For example, if a gamma of 0.80 is wanted, locate this value on the gamma scale; draw a straight line parallel to the development scale until it intersects the TIME-GAMMA curve; then drop a vertical line from this point to the development scale; and finally read the time of development required for a gamma of 0.80 – in this particular case, five minutes.

The time-gamma curve generally is derived from development tests made at 68 F, and a curve is required for every combination of emulsion and developer. Not only do different developers have different activities, but different emulsions develop at different rates. Data sheets often include time-gamma curves for the recommended emulsion-developer combinations.

EFFECT OF TEMPERATURE

The rate at which development takes place is increased as the temperature of the developer is raised. Assuming that the four-minute development curve in Figure 7 is the best for the emulsion X, the curves in Figure 9 illustrate the effect of increased temperature.

Since 68 F is the standard temperature for most black-and-white processing, the family of curves in Figure 7 was obtained by development at 68 F. As the temperature is raised, development occurs more rapidly, and therefore more silver is formed in a specified time of development. Similarly, lowered temperatures cause a slowdown in the formation of silver, and consequently lower density, gradient, and gamma are produced.

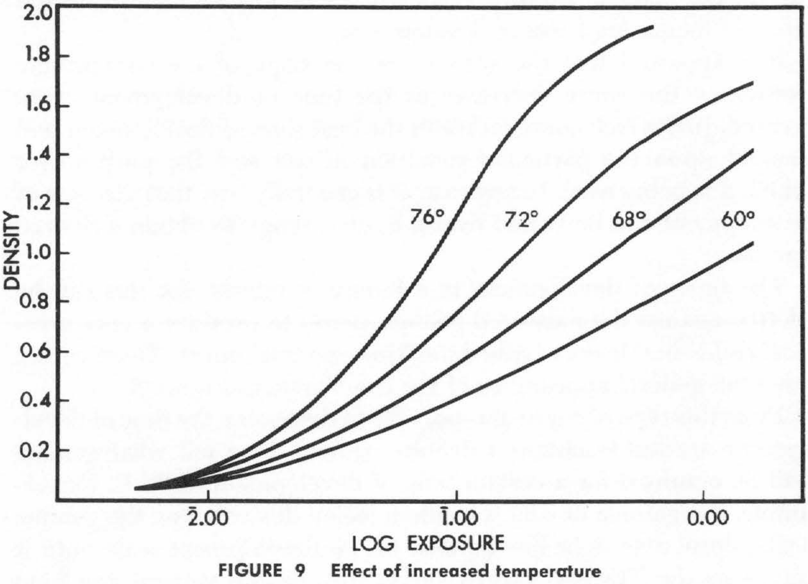


FIGURE 9 **Effect of increased temperature**

From the chemical viewpoint, a higher temperature affects the rate of chemical reactions, the rate at which solutions diffuse through the gelatin, and the extent to which chemicals ionize or dissociate in solution. These rates are usually increased by raising the temperature, and each plays a part in the final reaction. Actually, the effect of temperature is extremely complex, but controlled tests reveal the total effect insofar as it affects the practice of photography.

In practice, it is often desirable to know in advance the necessary adjustments in technique to allow or correct for temperatures other than normal. Actual experiments to obtain these data are seldom necessary, because the manufacturers have published data in a convenient form for reference.

For example, if the developer is at 74 F, what time of development at this temperature will produce the desired degree of development? For any specific combination of emulsion and developer, a time-temperature curve can be obtained if a series of tests is made, under controlled conditions, at a series of temperatures for a series of development times. From the test series, the time which gives the desired development is determined for each temperature and can be plotted on graph paper to provide the time-temperature curve.

Since, for emulsion X, the correct time of development is four minutes at 68 F, the standard temperature, the new time of development at 74 F will be three minutes. The rate of development is increased at the higher temperature, and therefore less time is required in the developer to obtain a given gamma, or degree of development.

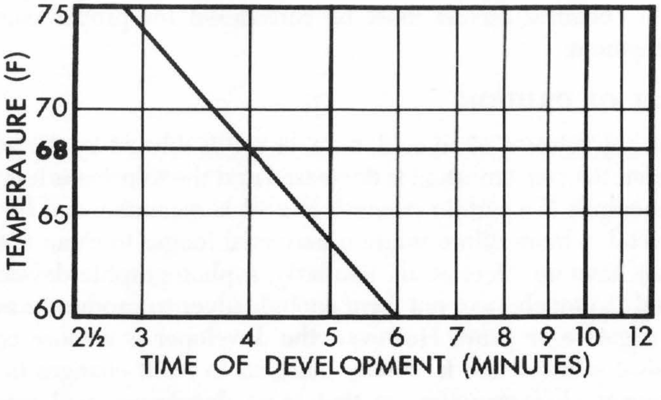


FIGURE 10 Time-temperature curve

EFFECT OF AGITATION

The importance of agitation has been mentioned before. If there is no agitation, a stagnant layer of solution forms along the emulsion surface. The solution is enriched in bromide, a restrainer, and is partially depleted of developing agent. Unless fresh unused developer is supplied to the emulsion surface, the development rate is slowed down.

Agitation of the developer solution disrupts the stagnant or quiescent layer of used developer and permits fresh developer to reach the emulsion. The method and extent of agitation employed will determine the effectiveness of the development. In any case, the agitation must be such as to provide a uniform rate of reaction over the whole emulsion area. *Agitation is generally extremely important in the first few seconds or minutes of development,* because during this period swelling of the gelatin and initiation of development take place. Very uneven effects may be obtained when the method and extent of agitation are not correct.

In the present practice of photography, processing is based usually on the data supplied by the manufacturer. These data are based on carefully controlled sensitometric tests, and if the data are to serve as a guide, correct time of development, temperature, and agitation must be observed by the photographer or technician. These factors are important for all combinations of emulsion and developer.

CHEMICAL FACTORS

In addition to the physical factors, such as time and temperature, certain chemical factors must be considered for proper control of development.

EFFECT OF DILUTION

When any solution of an acid, base, or salt is diluted by the addition of water, the concentration is decreased and the solution is less active. For example, if a certain strength of acid is recommended for cleaning metal, a more dilute solution may take longer to clean the metal or may have no effect at all. Similarly, a photographic developer, if diluted too much, may not form enough silver to produce a satisfactory negative or print. However, the developer is a more complex chemical solution and is usually buffered to resist changes in its development characteristics, so that most developers will tolerate a slight dilution without any significant change in activity.

On the other hand, some developers are compounded as stock solutions which are intended to be used at different dilutions for different purposes. In these cases, the amounts of chemicals used in the stock solution are sufficient to permit the recommended dilutions and produce developer solutions having the properties desired for the various uses.

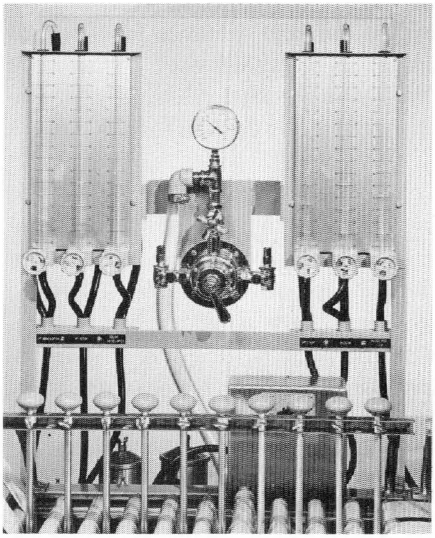
In general, a more dilute developer is less active and will either produce a weaker image in a given developing time at a given temperature or need a longer time to produce a given degree of development. Since photographic developers are rather complex chemical solutions and since different developers vary considerably in composition it is almost impossible to predict exactly the effect of dilution. Generally it is necessary to determine the effects by practical tests. Some developing agents are less susceptible to the effects of dilution than others, and the pH is more readily changed in some developers.

EFFECTS OF USE

So far, only the effects in fresh developer solutions have been considered. It was stated before that developers are compounded to allow the development of a considerable area of emulsion without appreciable change in the photographic image. How well a developer will do this determines the "exhaustion life" of the developer.

In most instances, the formula for a developer or any other photographic processing solution is worked out chemically so that a satisfactory image is produced not only on a single piece of film or paper but on several separate pieces processed in succession. This means that the quantities of individual chemicals in the formula must be in the correct ratio to produce (1) a satisfactory image in the first place and (2) a satisfactory image in each of a series of exposed films or prints, all of which received the same exposure. The final formula is the result of series of sensitometric tests, along with tests made under practical conditions. The sensitometric tests provide an accurate check on the condition of the solution at different stages in its use.

Exhaustion figures are usually given in terms of 8 by 10-inch sheets of film or paper per gallon of developer, or in terms of square feet of film or paper per gallon. Theoretically, they should represent actual working conditions, especially with respect to the proportion of the exposed area on the film or paper. This is important since the developer is exhausted according to the amount of silver developed. However, it is impractical to give a different exhaustion figure for each of the numerous applications. For each developer, therefore, the manu-



A system of continuous replenishment is used by large processing laboratories. The rate of replenishment is controlled by valves and flowmeters, such as those shown here.

facturer attempts to provide an average exhaustion figure which can serve as a guide in any particular operation.

The technique used in processing the photographic material has a very important bearing on the exhaustion life of a solution. For example, in tray processing the operator can drain each film or print before transferring it to the next tray or he can transfer it without drainage. In the latter case, more developer is carried out and fewer sheets can be developed. Consequently, with this technique it may not be possible to process as many sheets as indicated by the exhaustion figures. Because of the possible variations in processing technique, the stated exhaustion life usually includes a safety factor for handling, but it still should be used only as a guide.

REPLENISHMENT

In many applications, such as motion-picture film processing, it is important to maintain the developer properties without change throughout the processing of large quantities of film or paper or for long periods of time. This is accomplished by *replenishment*, which is the addition of chemicals to make up for the changes in the developer solution caused by use. In small-scale work, it is best to use the replenisher formula recommended by the manufacturer for the usual conditions of operation. In large-scale operations, as in motion-picture processing laboratories, it may be desirable to make chemical and photographic tests on the solution, and then adjust the concentrations of chemicals in the replenisher to suit the requirements of the particular situation.

The composition of the replenisher depends on the composition of the developer with which it is used. Generally, the replenisher will have the same concentration of sulfite as the developer, but higher concentrations of the alkali and developing agents that are used up in the development reaction. Restrainers, such as potassium bromide, are usually omitted entirely from the replenisher. In some cases, a concentrated, or stock, solution of the developer itself is used as the replenisher, but this is not advisable unless it is specifically recommended by the manufacturer.

Usually, the concentration of the replenisher is adjusted so that it keeps the activity constant when sufficient solution is added to the developer to replace that absorbed and carried out by the film. However, since this volume will depend on how long the film is allowed to drain when it is removed from the developer, it is often necessary to make some adjustments to fit particular operating conditions. In any case, the replenishment technique should be carefully planned and tested before it is put into actual practice. Also, to make sure that the replenishment rate is properly adjusted, the activity of the developer should be watched carefully during use.

RINSE BATHS

If the desired degree of development is to be obtained, the chemical reactions in development must be stopped quickly after the correct development time has been reached. Rinse baths are used for this purpose.

With some emulsion-developer combinations, plain running water is adequate, but in many cases an acid is added to make the bath more effective in stopping the development action quickly and uniformly. Such an acid rinse is generally called a "stop bath" and stops development by neutralizing the alkali or activator in the emulsion layer. The stop bath prevents brownish-colored stains sometimes formed by the action of the oxygen in the air on the alkaline developer on the surface of the film or print and also keeps alkaline developer from affecting the hardening action of the fixing bath. The swelling of the gelatin in the emulsion is also decreased when the film or print is immersed in the acid solution.

An acetic acid solution is the most commonly used stop bath. The strength of the solution should not be too great for two main reasons:

(1) it can affect the physical condition of some photographic paper supports in such a manner that they become too brittle during drying or storage, and (2) it can react with the sodium carbonate in some developers to form carbon dioxide gas within the emulsion structure and cause blisters. Under very bad conditions, an excessively acid bath can liberate sulfur dioxide gas from the sulfite in the developer.

An acid stop bath can tolerate a certain amount of alkali carried into it by the developed films or prints before its effectiveness is lost. This can be checked by the use of indicator dyes that change color when the acidity of the bath has been decreased to the danger point. Generally, a fresh acetic acid stop bath has a pH of approximately 3.5; a used or exhausted bath, a pH of about 5.5. Film stop baths can be brought back to the original pH value by the addition of 28 percent acetic acid. This replenishment is not recommended in paper processing, however, because reaction products which accumulate in the bath during use may cause a variety of mottle patterns if the print is subsequently toned.

PRACTICAL SUGGESTIONS

This whole discussion of development can be resolved into a set of rather simple rules for the photographer or technician as follows:

1. Use developer formulas recommended for the product employed.
2. Compound developer accurately according to either published formulas or instructions on packaged developers.
3. Use chemicals of highest purity.
4. Dissolve the chemicals in the order listed in the published formula, and make sure that each is fully dissolved before the next is added.
5. Adopt a standard development procedure with relation to time of development, temperature, agitation, and the quantity of material to be processed.
6. Use the degree of development best suited to the type of work and equipment to be used. This must be based on previous experience or tests in which published data can be used as a guide.
7. Rinse and fix according to recommended procedure.

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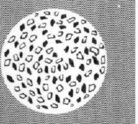
Photographic Fixing Baths



The latent image formed during exposure is developed in the photographic developer to produce the visible image. At this stage in processing, the emulsion still contains most of the unexposed silver halides. The purpose of the fixing bath is to remove the unexposed silver halides from the emulsion and thereby make the image more permanent.

• The importance of the fixing bath in photography is shown by the fact that a third of a century elapsed after the announcement of the production of the first photographic pictures by Wedgewood and Davy in 1802 before a practical method of producing permanent pictures was discovered. As soon as a satisfactory fixing agent was available, progress in the development and application of the photographic process was rapid.

A suitable fixing agent for silver halide emulsions should meet the following requirements: (1) it must dissolve the silver halides completely, (2) it must form salts with the halides that are soluble in the fixing bath itself and are stable when diluted so that they will not decompose during washing, (3) it must not attack gelatin, and (4) it must not affect seriously the silver grains of the developed image. There are several compounds that will dissolve silver halides, but most of them do not meet all of the above requirements. Some of these are sodium sulfite, ammonia, potassium iodide, thiourea, and the cyanides. Only the thiosulfates come sufficiently close to meeting all the requirements to be of interest in general photography. Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, and ammonium thiosulfate, $(NH_4)_2S_2O_3$, have proved to be most practical both chemically and economically.

CHEMISTRY OF FIXATION

The behavior of compounds such as silver bromide, which are only very slightly soluble, can be described by an equation which is very similar to that given in Chapter VII for the dissociation of water:

$$[Ag^+] \times [Br^-] = K$$

As before, this means that the product of the concentrations of silver and bromide ions is a constant. Therefore, if the concentration of the free silver ions is reduced by some means, the concentration of the bromide ions can increase, which means that more silver bromide can dissolve.

The thiosulfates form very stable complex compounds with silver ions, and thus effectively reduce the concentration of free silver ions in the solution. This makes it possible for the silver bromide and other silver halides to continue to dissolve. Thus, sodium and ammonium thiosulfates can act as silver halide solvents.

Chemical studies indicate that there are probably several of these thiosulfate-silver compounds existing in a used fixing bath and that their composition changes progressively as more of the silver halides are dissolved. In general, these compounds are soluble in the fixing bath and in water, and they do not decompose when diluted with water during the washing operation. There is some evidence, however, that one of these complex compounds may be somewhat less soluble than the others, or at least is not removed as readily by the wash water. This compound is formed when the total silver concentration in the bath is increased beyond a certain point. The practical effects of this will be discussed later.

OTHER INGREDIENTS

In addition to the sodium or ammonium thiosulfate, called "hypo" in the photographic trade, practical fixing baths contain a number of other ingredients which perform various special functions.

Acid. In order to avoid various possible troubles, the fixing bath must be able to neutralize any of the alkaline developer solution that might be carried in by the photographic material. To accomplish this, an acid must be added. However, when a strong acid is added to a hypo solution, the hypo is decomposed to form a fine suspension of sulfur in the bath. A film fixed in such a solution becomes opalescent on drying, because the "colloidal sulfur," as it is known, enters the emulsion structure during fixation and is not removed during washing. An opalescent negative cannot be printed satisfactorily, or at best only with considerable difficulty. Fortunately, a weak acid, such as acetic acid, produces colloidal sulfur very slowly and can be used in the fixing solution with the addition of a preservative to prevent the formation of the sulfur.

Preservative. The most commonly used preservative is sodium sulfite (Na_2SO_3) which, in solution, reacts with colloidal sulfur according to the equation

$$Na_2SO_3 + S = Na_2S_2O_3$$

to form sodium thiosulfate. Actually, the chemistry involved is more complex than the equation indicates, but this is a satisfactory representation of the final result. *Note:* Sodium sulfite is also used as the preservative in photographic developers, but its action in this case is quite different from that in the fixing bath.

Hardener. In order to prevent excessive swelling and softening of the emulsion during washing, with the consequent danger of mechanical injury, a hardening agent is generally used in the fixing bath. Potassium alum is the most widely used hardener for this purpose.

Buffer. To be most useful in practice, a fixing bath should be able to withstand the addition of a considerable amount of developer with only a small change in pH, that is, the solution must be *buffered* and at the same time have a large reserve acidity. Therefore, acetic acid and sodium sulfite are used in sufficient quantity and in the correct relative amounts to satisfy these requirements. (See fixing-bath formula on page 78). The addition of a hardener, such as potassium alum, also has a definite effect upon the buffering of the solution. Boric acid is used, in addition to acetic acid, to improve the buffer action and antisludging characteristics.

In practice, it is important to have available fixing baths which prevent the formation of colloidal sulfur, form a minimum amount of sludge, and are well buffered in the pH range in which alum is an effective hardening agent.

TYPES OF FIXING BATHS

Fixing baths are classified, primarily on the basis of their composition, into three general types: plain, acid, and acid hardening.

Plain baths contain hypo, with no other constituents. The pH of these baths is approximately 5.2. Since the plain hypo solution is not buffered, the pH changes very rapidly, and the solution will not tolerate much addition of either developer or stop bath. Developer raises the pH of the bath rapidly, and consequently it cannot stop development effectively. Stop bath lowers the pH rapidly, and colloidal sulfur is formed in the fixer. From a practical viewpoint, this type of bath is not satisfactory for the processing of quantities of film or paper. Actually, it is more useful in experimental work where a single test strip or sheet is fixed and the solution is then discarded.

Acid Baths. In order to increase the useful life of a hypo solution, acetic acid and sodium sulfite are added. Sodium bisulfite is sometimes used in place of the acetic acid in these baths, since it is an acid salt ($NaHSO_3$). Kodak Fixing Bath F-24 is representative. (The pH of this type of bath is approximately 4.6 to 5.0.) Such baths are useful when additional hardening of the emulsion is not required and are especially indicated in some photographic applications where rapid washing is important (see page 109). In general, however, acid hardening baths are used for fixing both films and papers.

Acid Hardening Baths. The most commonly used bath of this type is the potassium alum bath buffered to have a pH of approximately 4.1. At this low pH value, these baths have a much greater exhaustion life than baths of higher pH and are of particular interest in the large-volume production of negatives and prints. Fixing baths containing boric acid were introduced primarily to provide a solution with improved hardening and exhaustion characteristics. Kodak Fixing Bath F-5 is typical.

Kodak Fixing Bath F-5

Kodak Fixing Bath F-5 is recommended for general use; if prints tend to stick to belt or drum dryers; or if prints become softened in toning operations. This bath has the advantage over the older type of fixing baths, which did not contain boric acid, that it gives much better hardening and has less tendency to precipitate a sludge of aluminum sulfite.

	Avoirdupois—U. S. Liquid	Metric
Water, about 125F (50C)	80 ounces	600 cc
Kodak Sodium Thiosulfate (Hypo)	2 pounds	240.0 grams
Kodak Sodium Sulfite, desiccated	2 ounces	15.0 grams
Kodak Acetic Acid, 28%	6 ounces	48.0 cc
Kodak Boric Acid, crystals	1 ounce	7.5 grams
Kodak Potassium Alum	2 ounces	15.0 grams
Cold water to make	1 gallon	1.0 liter

For processing in tropical regions or at elevated temperatures, a potassium alum fixing bath may not provide adequate hardening of the emulsion. Chrome alum fixers are indicated in some of these cases because this hardener is more effective than potassium alum. However, there are some practical difficulties not encountered with the potassium alum baths. The pH must be maintained between the values 3.1 and 3.8; otherwise, above pH 3.8, there is formed a heavy gelatinous precipitate of chromium hydroxide [$Cr(OH)_3$] which is difficult to remove from film surfaces. In order to reach this pH range, a strong acid, such as sulfuric acid, must be used, and the solution has very little buffering action. In practice, it is usually too bothersome to maintain this rigid control of pH. It is also significant, from a practical viewpoint, that these baths change with age even when no other chemicals are introduced by use.

Chrome alum fixing baths are not used in processing photographic prints, because the green solution tints the paper stock and the additional hardening action is not usually required because paper emulsions are generally hardened to a greater extent in manufacture than film emulsions.

TIME REQUIRED TO FIX A FILM OR PRINT

The manufacturers of photographic materials and chemicals recommend in their data sheets and instruction sheets the times for which their products should be fixed. These recommendations are based on the results of laboratory tests and trade experience in the use of fixing baths. All silver halide emulsions are opalescent because of the halides suspended in them. As the fixer dissolves the silver halides, the emulsion becomes clear. The time required for an emulsion to just clear is known as the "time to clear" and provides the basis for the recommended fixing times.

Chemically, the halides are dissolved to form complex silver compounds, but some of these may be insoluble in water and will not wash out. Therefore, it is necessary to treat the emulsion long enough to assure the formation of compounds that are soluble in water. In general, this can be assured by allowing *twice* the time to clear. Longer treatment does not make the removal of the complex silver compounds any easier; in the case of papers, it may actually make it more difficult.

On this basis, it is found that different types of emulsions are fixed as follows:

paper emulsions	45 to 70 seconds
positive-film emulsions	45 to 60 seconds
negative-film emulsions	2 to 7 minutes

The time to clear depends upon the thickness of the emulsion and the particular silver halides in the emulsion. For instance, contact-paper emulsions are quite thin and, in general, contain silver chloride, which is finer grained and more soluble than silver bromide or iodide. Negative emulsions are much thicker and contain silver bromide and, in some cases, silver iodide as well. More specifically, a paper of the Kodak Azo type will clear in 15 to 20 seconds, while Kodak Tri-X Film clears in about three minutes.

As more and more film or paper is fixed in a bath, more silver is added to the bath in the form of complex silver compounds. The result is a slower-working fixer which requires a longer time to clear an emulsion. There are limits to the amount of silver that can be added to a fixer. When the concentration reaches a certain amount there are formed some relatively insoluble compounds which cannot be removed from the emulsion by washing. It is therefore necessary to discontinue the use of a fixing bath before it reaches this condition. In view of this progressive change in the composition of a fixer, the recommended fixing time must be increased, at least, to include the time equal to twice the time to clear in a used bath.

In fixation, as in development, agitation is extremely important. The films or prints should be kept well separated so that the entire surface is in continuous contact with fixer. Unfortunately, in practice this procedure is not always followed, and it is necessary to include in the recommended fixing time a safety factor to allow for inadequate agitation and separation.

The recommended fixing times are therefore considerably longer than twice the time to clear, because of (1) the build-up of silver in the fixing bath and (2) the need for a safety factor to allow for poor technique.

EXHAUSTION LIFE OF A FIXING BATH

When the silver content of a fixer has reached the permissible limit, the bath is said to be exhausted. This means, from a practical viewpoint, that a certain area of film or paper can be processed before a bath should be discarded. Quite often the manufacturers state an exhaustion life for a bath, usually in terms of sheets or rolls per gallon. Such figures are only approximate and serve as a guide to the technician. This is so because it is impossible for the manufacturer to know or to predict exactly how much silver will be added to the bath from each exposed sheet or roll of emulsion. For example, if line sketches or drawings are being copied, most of the silver halide is exposed and only those areas corresponding to the lines are unexposed. Thus, most of the silver in the emulsion is developed to metallic silver and very little silver halide is dissolved by the hypo. On the other hand, a negative of a small object in front of a dark background would use comparatively little of the silver for the image, and considerably more silver halide must be dissolved in the fixer. Therefore, in the latter case, the concentration of silver in the fixer will reach the limit after fewer sheets have been processed.

Another important factor related to the useful life of a fixer is dilution of the solution by the carry-over from either the developer or the stop bath. Dilution can affect the exhaustion life because the concentration of chemicals is lowered. The buffer capacity may be affected and the rate of fixing reduced.

It is possible to test a fixing bath rather easily for silver concentration to determine when the bath is exhausted and should be discarded. The main advantage in testing the bath is to allow full use of the bath and still assure good fixation under any specific working conditions. Any test for silver should be designed to indicate accurately when the silver concentration in a fixing bath has reached the limit above which the silver compounds cannot be removed readily from the film or print or above which staining occurs readily. In the case of prints, it has been found that up to 2.0 grams per liter of silver in the bath can be tolerated. At this concentration the bath should be discarded. The test should provide a very rapid and positive indication that the silver concentration has reached this limit. The Kodak Testing Outfit for Print Stop Baths and Fixing Baths provides an excellent check on this condition in print fixing baths because a heavy yellowish precipitate is formed instantaneously at the above concentration. A great majority of the tests recommended in the literature for this purpose do not indicate the maximum amount of silver allowable but usually much lower concentrations. The result is to discard the bath before full use is made of it.

In the case of films, the most satisfactory test to determine the exhaustion of a fixing bath is the measurement of the time to clear. As the silver content increases in a fixing bath, the rate of fixation slows down and therefore the time to clear increases. By use of a standard film test strip for which the time to clear at the dangerous silver limit is known, the condition of a fixing bath can be determined readily with respect to silver concentration. Sodium thiosulfate baths usually contain about 6.0 grams per liter of silver when the above test is positive.

There are other changes that take place in a fixing bath during use. When no rinse bath is used, developer is carried by the film or prints into the fixing bath. The developer is quite strongly alkaline and, if enough is carried over, will eventually use up all of the acid. The amount carried over depends on the handling technique. The hardening action of the alum in the fixer is controlled by the pH, and when the pH increases to above 5.5, the hardener works less effectively. At this point, the bath should be discarded or the pH should be adjusted by the addition of more acetic acid in order to maintain the hardening action of the alum. For this reason, it is good practice to use an acid rinse bath which neutralizes the alkali in the developer before the films or prints reach the fixing bath.

It should be pointed out that the exhaustion of a fixing bath is not satisfactorily determined by foaming, frothing, or feel of the solution – criteria which have been suggested. Usually, by the time this occurs, the pH of the fixing bath is considerably too high for effective hardening action.

AMMONIUM THIOSULFATE VS SODIUM THIOSULFATE

Sodium thiosulfate was recommended in 1837 as a fixing agent and proved to be the most satisfactory bath, practically and economically. A few years ago, ammonium thiosulfate was made available, not in crystalline form, but as a 60 percent solution. When used in place of the sodium thiosulfate in fixing baths, it was found to fix silver halides more rapidly. The time of fixation was reduced as much as 50 percent for some negative materials. This was of interest in those applications where more rapid processing was desirable. The result was the introduction of rapid liquid fixing baths.

Because of their greater activity, these baths must be used with more care. If a developed print or film is left in a fixing bath for too long, the hypo may begin to dissolve the silver from the low-density areas of the image, especially in fresh acid baths. This effect occurs more readily with fine-grained emulsions, such as the silver chloride contact-print emulsions. It occurs much more readily in ammonium thiosulfate fixing baths. As a result, rapid liquid fixing baths are usually used at two different dilutions – one for film and another for paper. For example, Kodak Rapid Fixer is diluted with three parts of water for films and seven parts of water for prints. Even at these dilutions, and especially with prints, reduction of the silver image will occur more rapidly than in the usual sodium thiosulfate baths.

Chemically, ammonium thiosulfate also forms complex silver compounds when dissolving the silver halides from the emulsion. But more soluble complexes exist in these baths than in sodium thiosulfate baths when the silver concentration has reached 6.0 grams per liter. In fact, almost double this quantity of silver can be accumulated in an ammonium bath and still be removed from the emulsion by washing. The best criterion for judging the exhaustion point of these baths for film is the clearing time of the film. When the clearing time for any particular brand of film has increased to twice the time required to clear the same film in a fresh fixer, the fixing bath has reached the practical exhaustion point.

A PRACTICAL PROBLEM

The following question is often asked: Can the same fixing bath be used for the fixation of both films and prints? From the discussion of the exhaustion life of a fixing bath, it is apparent that prints cannot be fixed properly in a solution containing more than 1.5 to 2.0 grams of silver per liter. Therefore, both films and prints can be fixed in the same bath until the silver concentration reaches this quantity. Then, only films can be fixed in it until the film exhaustion point is reached. The only way to be certain that prints are not being fixed in an exhausted bath is to test the bath for silver just before it is used each time. This is particularly important if it is desirable to keep the prints for a long time. *The best procedure is to use separate baths for films and for prints.* For a specific setup and method of operation, the control test need be used only to determine the amount of film or paper that can be processed before the bath is exhausted.

TWO-BATH FIXATION

No matter what the reason is for making negatives or prints, an effort should always be made to provide the best conditions for complete fixation. In many applications, this is imperative because certain specifications for permanent records must be satisfied. The best and most economical way to accomplish this is with two fixing baths.

In practice, the most widely used technique requires that the films or prints be fixed in the first bath and then be transferred to a second bath. This means that all of the unexposed silver halides are dissolved in the first bath and therefore most of the silver is in the first bath. Any silver compounds left in the emulsion are removed in the second bath, and complete fixation is assured because the silver will always be in a form readily soluble in water and therefore easily removed by washing. The first bath is used until the exhaustion point is reached, when it is discarded. The second bath is then moved to replace the first one and is itself replaced by a fresh bath. This cycle can be repeated several times without the quantity of silver in the second bath building up to an objectionable value. Usually the number 8 by 10-inch films or prints per gallon recommended by the manufacturer is processed before the baths are changed. Not more than five cycles is suggested, and if this number of cycles is not used during a week's operating time, both baths should be changed at the end of a week. In many cases, two fixing baths used as above can effect savings in chemical costs amounting to almost 50 percent.

SILVER RECOVERY

The useful life of fixing baths can be extended if some means are provided for the removal of silver from the fixing bath. This can become important in processing operations involving large volumes of fixing-bath solutions, as in motion-picture film processing and paper processing in continuous photofinishing operations.

There are two general types of silver recovery systems used: those which require outside electrical current for operation, usually called the continuous "electrolytic" system and employed in large-volume operations; and those which operate on the metal displacement principle, in which the silver in the bath is plated onto another metal surface placed in the solution.

The metal displacement principle is the basis for two kinds of service systems commercially available. The first consists of cartridges filled with a suitable metal in the form of filings. The cartridge is attached to the outlet of a hypo tank, and the solution is allowed to percolate through the cartridge to the sewer. The silver is plated out in the cartridge and is recovered by chemical methods as pure silver.

The second system consists of flat metallic bars designed to fit in trays or tanks. The bar is used until it reaches a certain weight, when it is returned to the distributing company where the plated silver is recovered.

Still another system is used in some large cities. The exhausted fixing baths are placed in storage tanks and then collected by a service company which recovers the silver.

In any case, commercial silver recovery systems are employed only when some financial return is received. In other words, it is worth considering silver recovery only if there is some net gain financially after payment of rental or service charges.

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Reversal Processing

The development of an image on a negative or on a print made from a negative has been discussed. The reversal process produces a positive instead of a negative image on the material which received the original exposure, and thus eliminates the need for making a print.

• The reversal process forms a positive image directly or, in other words, a reproduction that looks like the original subject. It is used in the production of amateur movies, positive black-and-white transparencies for television, positive line reproductions in the graphic arts field and some color motion pictures, transparencies, and prints.

Although proper control of exposure and development in negative processing is desirable if you wish to obtain a good-quality negative, some variation in exposure or processing does not prevent the use of the negative for making prints. The range of contrast provided in photographic papers and the possibility of changing the printing exposure permit corrections of some errors in negative making. In other words, there is considerable exposure and development latitude in the use of most negative materials.

This is not the case in reversal processing, because a good-quality image can be obtained only when the exposure and first development are correctly balanced. Any variation from this balance will degrade the picture quality. Because of this dependence on the exposure-development balance, as well as possible image degrading effects in the other processing steps, reversal processing requires very careful control. It is for this reason that the manufacturers of both black-and-white and color-reversal products have generally processed these films for their consumers. In recent years, improvements in products, equipment design, and processing techniques have made it possible for the consumer to do his own processing, but close control is still a most important factor.

The chart in Figure 11 shows a comparison of the two processing systems with respect to the basic steps. In negative and print processing, the exposed silver halides are developed and then the undeveloped silver halides are removed by the fixing bath.

In reversal processing, the exposed silver halides are developed as before, then this negative silver image is removed in a bleach bath and the remaining silver halides are developed to form a positive image. This can be done by exposing them to light and then using a conventional developer. However, in some processes, the re-exposure is not necessary, because special fogging developers can be used to convert all of the remaining silver halide to silver without the use of light.

In reversal color processes, it is not necessary to remove the negative silver image before the second development. Instead, it can be left while the color developer produces a positive image consisting of silver and dye. Then the silver of both the negative and positive images is removed, leaving the desired image of colored dyes. This is frequently an advantage, because when the negative silver image is removed before the second development, the bleach bath must not affect the silver halides that are needed to form the positive image. When the silver is not removed until after the second development, the bleach bath is not limited by this requirement. However, this is possible, of course, only when the final positive image is composed of dyes, not silver.

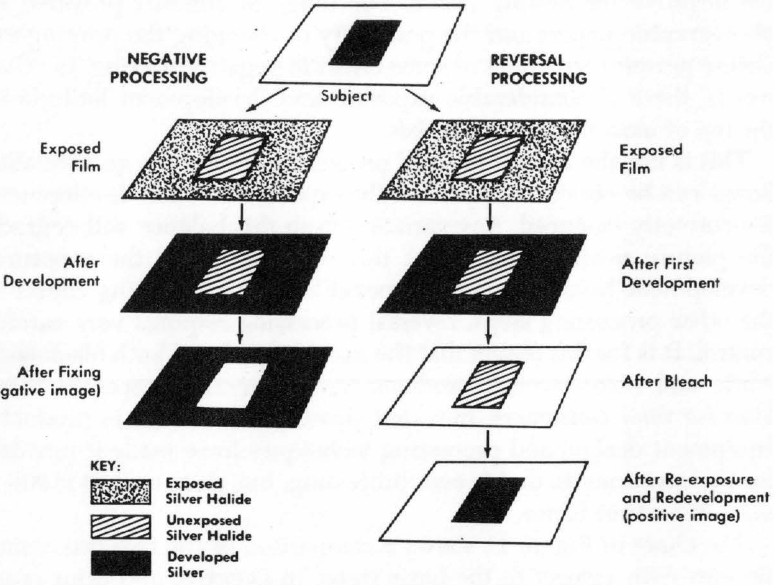


FIGURE 11 Comparison of negative and reversal processing systems.

BLEACH BATHS

The purpose of the bleach bath is to convert the negative-image silver formed in the first development either to a soluble silver salt that can readily diffuse from the emulsion into the bath or, in color processing, to a silver salt that can be dissolved in a subsequent bath.

A commonly used bleach bath in black-and-white reversal processing contains potassium dichromate and sulfuric acid. The silver image is converted to the soluble silver sulfate compound, most of which diffuses from the emulsion into the bath. The subsequent water rinse removes the residual silver sulfate and bleach bath chemicals from the emulsion. The chemical reactions in the bleach bath may be expressed as follows:

$$\begin{array}{lllll} 6\,Ag & + & K_2Cr_2O_7 & + & 7\,H_2SO_4 \; = \\ \text{silver} & & \text{potassium} & & \text{sulfuric} \\ \text{image} & & \text{dichromate} & & \text{acid} \end{array}$$

$$\begin{array}{lllllll} 3\,Ag_2SO_4 & + & Cr_2(SO_4)_3 & + & K_2SO_4 & + & 7\,H_2O \\ \text{silver} & & \text{chromic} & & \text{potassium} & & \text{water} \\ \text{sulfate} & & \text{sulfate} & & \text{sulfate} & & \end{array}$$

Chemically, this is just the reverse of the development reaction, because the metallic silver is oxidized to silver sulfate by the dichromate in acid solution, while the potassium dichromate is reduced to chromic sulfate. Insufficient bleaching results in an undesirable filling-in of the picture highlights, that is, some of the negative-image silver may be left in the emulsion.

The agent used in bleach baths for color processes should be capable of oxidizing the silver in the presence of a halide without attacking the dye image. Oxidizing agents, such as potassium permanganate or potassium dichromate, usually attack the dye image. A common bleach bath used after second development in color processing contains potassium ferricyanide and potassium bromide. The oxidizing agent converts the image silver to silver bromide which is then removed by fixing in hypo. The reaction of the ferricyanide with the image silver can be shown by the equation:

$$Ag + Fe\,(CN)_6^{\equiv -} + Br^{+} \longrightarrow AgBr + Fe\,(CN)_6^{==}$$

The metallic silver is oxidized to silver ions, which immediately combine with the bromide ions to form silver bromide, and the ferricyanide is reduced to ferrocyanide. The silver bromide is dissolved in hypo in a subsequent fixing operation.

RINSE BATHS

It is important to avoid contamination of the various baths used in reversal and color processing. Consequently, it is necessary to make considerable use of rinse baths, even though they increase the number of processing steps and lengthen the time required for the process.

Rinses are used to remove the chemicals absorbed by the emulsion in one bath in order to avoid undesirable effects in the succeeding bath. For this basic purpose, plain running water is quite efficient. Frequently, however, certain chemicals may be added to a rinse to make it more effective in stopping the action of the previous bath and in neutralizing or removing certain of the chemicals.

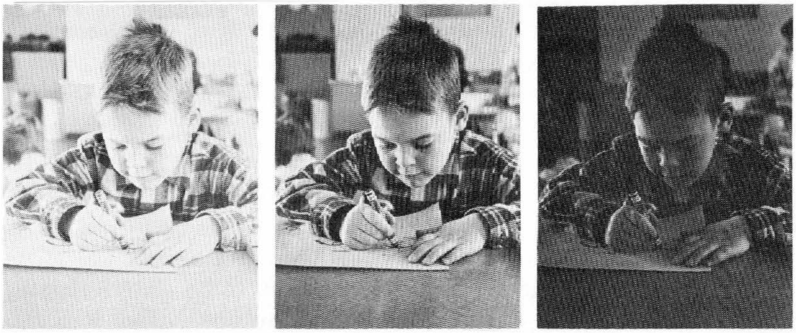
In negative and print processing, an acid stop bath is often used to stop the development action quickly and uniformly and to keep the alkaline developer from affecting the hardening action of the fixing bath.

In reversal processing, each chemical operation is usually followed by a water rinse, at least. However, following the dichromate bleach used to remove the image silver formed in the first development, a solution of sodium sulfite or sodium bisulfite is employed to react with any residual dichromate which would interfere with the action of the second development. A rinse bath used for this purpose is known as a "clearing bath." The chemical composition of this bath depends upon the processing cycle, particularly the type of bleach bath used. It is therefore imperative to use the clearing bath or other rinse baths specified in any particular process.

In the black-and-white reversal process, practically all of the silver halides are exposed and developed in the first and second developers. Therefore, a fixing bath is not required for removal of undeveloped silver halides as in negative-positive processing cycles. Following second development, however, a rinse bath is required to neutralize the alkali from the developer and to harden the gelatin in the emulsion to make it more resistant to subsequent handling. The bath used for this purpose is frequently a conventional acid hardening fixing bath.

CONTROL OF REVERSAL PROCESSING

No one series of reversal processing solutions can be used to obtain direct positive images on all photographic materials. The process must be worked out in detail with respect to solution composition and the times of treatment in each solution for a specific product. Special



Effects of exposure and development variations in the reversal process.
Left — Result of overexposure or overdevelopment in the first developer.
Center — Correct exposure and development.
Right — Result of underexposure or underdevelopment in the first developer.

reversal-type emulsions are manufactured for black-and-white applications, such as amateur movies, and the processing procedure worked out by the manufacturer should be followed closely.

The exposure must be correct. Too much exposure produces a thin picture in which highlight detail is lost, as, for example, in the fine tonal range in the face of a person. Since the positive image must be formed from the silver halides left after the negative image has been developed, it is obvious that overexposure will result in the removal of too much of the silver required for the positive image. Similarly, too little exposure will leave too much silver for the positive image and it will be too dark. Remember that these effects are just the opposite to those obtained in negative development, where overexposure, for example, produces a darker-than-normal negative. There is very little exposure latitude in a reversal process, and the camera exposure must be correct if good results are to be obtained by the recommended processing procedure.

The first development is critical, and it is essential that instructions be followed closely for time of development and agitation. Overdevelopment and underdevelopment give results similar to overexposure and underexposure. The time of development at a specific temperature will vary somewhat according to the method of processing, e.g., tray, reel and tank, small tanks, or rewind processing equipment, because of the differences in the effective agitation. The published instructions should be considered as a starting point and guide. A few trial-and-error experiments may be necessary to determine the slight variation required to obtain acceptable results with any particular equipment. However, in those cases where the manufacturer has prepared instructions for reversal processing in specific equipment, good results should be obtained if all of the factors are carefully controlled according to specifications.

In most of the steps following the first development, the chemical action should go essentially to completion. Therefore, in black-and-white processing, the control of time and temperature in these steps is not particularly critical so long as the following three general rules are observed:

(1) Do not allow one chemical to contaminate another,

(2) Use adequate washing between solutions to be certain that all residual chemicals are removed from the emulsion before it is immersed in the next solution, and

(3) Allow the full recommended time of treatment in each of the solutions.

In color processing, variations in the conditions of any of the steps are likely to have some effect on the color balance between the three final dye images. Therefore, within the limits recommended for the particular process, the temperature, time, and agitation must be carefully controlled in all steps.

REPLENISHMENT OF SOLUTIONS

Replenishment of the developers and other solutions can be accomplished successfully if adequate tests can be made. For this reason, replenishment usually is practical only for large-volume continuous-processing operations. For the amateur, it is preferable to use fresh solutions as suggested in the instructions, because exhausted solutions are almost certain to cause unsatisfactory results.

13

Practical Color Processes

Most of the color processes now in general use are based on dye-forming development. They include both negative-positive and reversal systems.

• The Kodachrome Process, which was the first widely successful color process, is a reversal system which yields positive color transparencies on the film exposed in the camera. It utilizes color development, with the dye couplers in the developer solutions. Thus, three different color developers are necessary, and the action of each developer must be precisely controlled so that it affects only the correct one of the three emulsion layers of the film. Consequently, Kodachrome processing is practical only in large plants equipped with elaborate control devices and operated by highly trained technical specialists.

KODAK COLOR MATERIALS FOR CUSTOMER PROCESSING

The introduction of the incorporated-coupler color materials has made it practical for individual photographers, studios, photofinishers, and scientific and industrial laboratories to process their own color photographs. A full line of color materials is now supplied by the Eastman Kodak Company for making either color transparencies or color prints, by either a reversal or a negative-positive process. These materials, and the designations of the chemical processes to be used with them, are summarized in Table IV.

TABLE IV

Material	*Process*
Kodak Ektacolor Film, Type B	B-41
Kodak Ektacolor Film, Type S	C-22
Kodacolor Film	C-22
Kodak Ektachrome Film (Process E-1)	E-1
Kodak Ektachrome Film (Process E-2)	E-2
Kodak Ektacolor Print Film	C-22 or B-41
Kodak Color Print Material, Type C	P-122
Kodak Color Print Material, Type R	P-111

Negative-Positive Systems: Kodak Ektacolor Films (in sheets) and Kodacolor Film (in rolls) produce color negatives, from which color prints can be obtained on Kodak Color Print Material, Type C or color transparencies on Kodak Ektacolor Print Film. All of these materials require color development, and they have the dye couplers incorporated into their emulsion layers. The essential steps in the processing of these materials include: development of the exposed silver halides to form silver images and, simultaneously, the dye images in the three emulsion layers; bleaching of the silver in a special bleach bath; and removal of both the unused original silver halides and the bleached negative image in a fixing bath. Certain other supplementary treatments and, of course, rinses or washes between the various steps are also needed.

Outlines of the actual processing steps are shown in the following table.

TABLE V

Kodak Color Process C-22 Kodak Ektacolor Film, Type S Kodak Ektacolor Print Film Kodacolor Film	*Kodak Color Process B-41* Kodak Ektacolor Film, Type B Kodak Ektacolor Print Film	*Kodak Color Print Process P-122* Kodak Color Print Material, Type C
1. Developer	1. Developer	1. Developer
2. Stop Bath	2. Stop Bath	2. Stop Bath
3. Hardener	3. Hardener	3. Fixer
4. Wash	4. Wash	4. Wash
5. Bleach	5. Bleach	5. Bleach
6. Wash	6. Wash	6. Wash
7. Fixer	7. Fixer	7. Hardener Fixing Bath
8. Wash	8. Wash	8. Wash
9. Remove water droplets by wiping or with Kodak Photo-Flo Solution	9. Bathe in Kodak Photo-Flo Solution plus ¾ oz. Kodak Formaldehyde per gal.	9. Hardener
10. Dry	10. Dry	10. Wash
		11. Buffer
		12. Dry

Reversal Processes. The Kodak Ektachrome Processes E-1 and E-2, for color transparencies, and Kodak Color Print Process P-111, follow the general pattern for reversal processing, but they differ in a number of details. The basic steps include: reduction to silver, in the first developer, of the silver halides exposed in the camera or printer; exposure of the remaining undeveloped silver halides; development in the color developer to form the proper quantities of the three dyes; bleaching of the developed silver back to silver bromide; and removal of the silver bromide in a fixing bath. The various additional steps needed in the practical processes, such as stop bath, hardeners, and the various rinses and washes, are shown in the following table. It will be seen that there are some differences in the order of the steps between the Color Print Process, P-111, and the Ektachrome Processes. One important difference is in the point at which the reversal exposure is given. In the Ektachrome Processes, the films must be

TABLE VI

Kodak Ektachrome Process E-1	*Kodak Ektachrome Process E-2*	*Kodak Color Print Process P-111*
1. First Developer	1. First Developer	1. Prewet
2. Rinse	2. Rinse	2. First Developer
3. Hardener	3. Hardener	3. First Stop Bath
4. Reversal Exposure	4. Reversal Exposure	4. Wash
5. Wash	5. Wash	5. Reversal Exposure
6. Color Developer	6. Color Developer	6. Color Developer
7. Wash	7. Wash	7. Hardener Stop Bath
8. Clear	8. Clear	8. Wash
9. Rinse	9. Rinse	9. Bleach
10. Bleach	10. Bleach	10. Wash
11. Rinse	11. Rinse	11. Hardener Fixing Bath
12. Fix	12. Fix	12. Wash
13. Wash	13. Wash	13. Stabilizing Bath
14. Remove water droplets by wiping or with Kodak Photo-Flo Solution	14. Stabilizing Bath	14. Rinse
15. Dry	15. Dry	15. Dry

re-exposed *before* they are placed in the wash water following the hardener. In the Color Print Process, on the other hand, the re-exposure is given after a thorough wash. It should also be pointed out that, although the Ektachrome Processes E-1 and E-2 have exactly the same number and order of steps, they use different solutions, except for the hardener and the clearing and fixing bath.

Since the final images are composed of dyes, all of the silver formed by both developers must be removed. Therefore, the bleach is not used until after the color development, and it is followed by a fixing bath instead of the clearing bath needed in black-and-white reversal processes.

CHOICE OF SOLUTIONS

It is important to note that while the baths in the various processes perform similar functions, they do not have the same chemical compositions. The various processing solutions *must* be closely matched to the characteristics of each color material and the other solutions used in the process. Very extensive experimental testing is required to determine the best combination and proportion of chemicals in each series of processing baths.

Also, the processing conditions, such as temperature, times of treatment, and agitation, must be closely controlled to insure satisfactory results. Each color material has three different emulsion layers to be processed in proper balance, and the proper proportions of three different dyes must be produced to form the final image. As a result, a change in any processing step is likely to have an important effect on the final result. In all cases, the formulas have been worked out to provide the best concentration, time of treatment, and pH for most efficient treatment. Any attempt to vary the recommended procedures beyond the stated tolerances is almost certain to cause difficulties of one kind or another.

PREPARATION OF SOLUTIONS

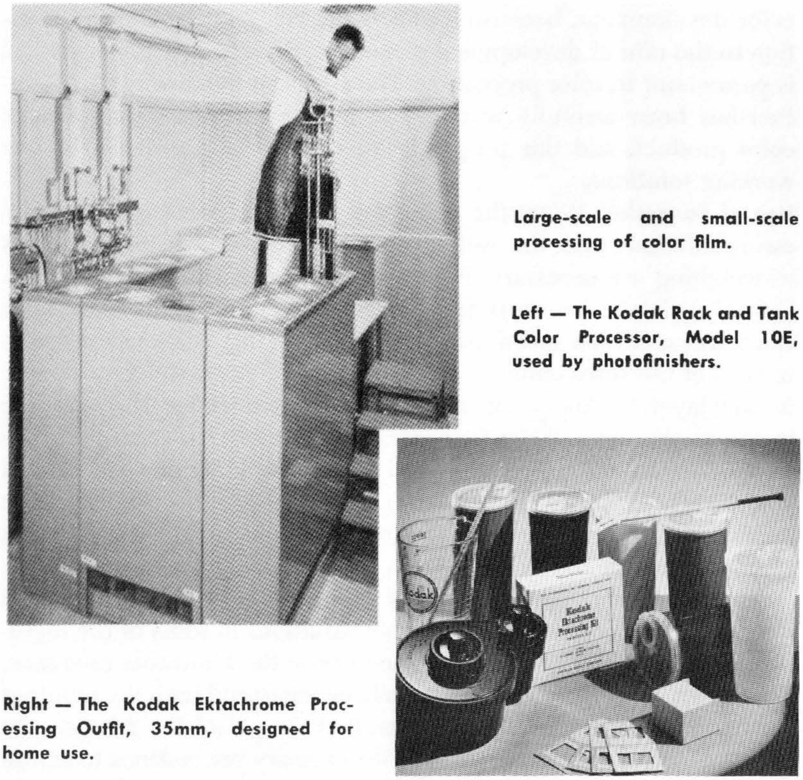
In these color processes, the chemical solutions employed are much more complex than those required for black-and-white processing, especially the developer solutions. Similarly, the chemistry of color development involves many more complex reactions, and consequently the composition of the solutions must be more carefully controlled with respect to the quantities of each chemical, the mixing of these chemicals, and the properties of the solutions, such as the pH and the specific gravity. The pH value is particularly significant in color development, because it affects the coupling reaction in addition to the rate of development of the silver image. Chemical control is paramount in color processing. The chemical balance in each solution has been carefully worked out by the manufacturer for each color product, and this proper balance must be maintained in the working solutions.

Use of Formulas: When the attempt is made to compound the processing solutions from the individual ingredients, very close tolerances in weighing are necessary if good color images are to be obtained. Variations in the concentration of a single chemical in these formulas can affect emulsion speed, maximum density, fog, color balance, etc, in each of the three emulsion layers and usually to a different degree in each layer. Ordinary scales usually recommended for photographic purposes are not sufficiently accurate, especially for measuring the developing agents and alkalies and any constituents that are used in very small quantities. In the latter case, in fact, the chemicals are generally measured by volume from dilute solutions, as with the potassium iodide in the formula on page 57.

As mentioned previously, the pH values of the developer solutions are quite critical. Because of possible variations in some of the ingredients, the pH of a solution may be outside the allowable tolerance, even when all of the chemicals have been measured with the required accuracy. Therefore, it is imperative that the pH of the solutions be checked with a pH meter, taking the necessary precautions to assure an accurate reading, and be adjusted as necessary according to the instructions for the formula.

Prepared Chemical Kits: These complications can be avoided by the use of the prepared chemical kits which are supplied for the various color processes. The manufacturer not only uses high-precision mixing procedures but also has available adequate facilities and skilled personnel to test and, if necessary, to adjust each batch in order to assure that the processing solutions prepared from each kit will have the specified characteristics for successful color processing.

As a result, the use of these prepared chemical kits is actually more economical for the individual user, because they avoid the necessity for careful testing and adjustment of each solution. The only precaution is that, in making up the solutions, the instructions for mixing must be followed carefully to be certain that each chemical is completely dissolved. Undissolved chemical in a bath can disturb the chemical balance of the solution and produce undesirable effects in the developed color image.



Large-scale and small-scale processing of color film.

Left — The Kodak Rack and Tank Color Processor, Model 10E, used by photofinishers.

Right — The Kodak Ektachrome Processing Outfit, 35mm, designed for home use.

PROCESSING CONTROL

The use of the prepared chemical kits makes color processing quite practical and relatively easy, because the only controls necessary during the processing cycle involve times, temperatures, and agitation. All that is required is suitable processing equipment and an accurate thermometer. For example, in processing Kodak Ektachrome 35mm films, the Kodak Day-Load Tank and Kodak Process Thermometer are adequate.

Temperature. The rate at which reactions take place between chemicals is affected by the temperature of the solution. The rate of reaction decreases or increases, respectively, as the temperature is lowered or raised. As stated before, the processing of color products, especially the development, involves a number of complex chemical reactions, some being more sensitive to temperature changes than others. In the reactions between the different dye couplers and the oxidation product of the developing agent, the relations between the various reaction rates may be considerably different at temperatures lower or higher than these specified. Therefore, the proportion of the dyes formed in the three layers will be incorrect, and color balance and color contrast will be wrong. It should be apparent, therefore, that a specified temperature should not be changed.

Careful control of the temperatures of all solutions in the processing of color products, whether in reversal or negative-positive processing, must be employed. In the other solutions, there are not so many reactions involved as in the color development, but the rate of reaction at a specified temperature in one solution freqently is directly dependent on the reactions of the other solutions in the cycle. Do not change the temperatures specified.

Time of Treatment. The length of time specified for the chemical treatments is especially important in color processing, because it is almost impossible to compensate for mistakes. Some defects that can result from too short or too long times of treatment include: lower or higher gamma and contrast; too little or too much dye in some or all of the layers; and stains of various kinds, caused by incomplete removal of reaction products from the emulsions.

Agitation. The degree and method of agitation employed is dependent to a very large extent on the design of the processing equipment. Usually, the manufacturer suggests specific equipment and recommendations for agitation. It may be necessary to make minor changes in the procedure to adjust the agitation to equipment slightly different in design from that suggested by the manufacturer. In general, too little agitation can produce nonuniform processing. Although the use of excessive agitation is usually not so serious as too little agitation, it is possible for it also to cause nonuniform results as well as to overdevelop the film slightly. In any event, continuous and vigorous agitation during the first 15 seconds in a developer is essential.

Roll-film tanks should be designed so that removal of the film from the reel for re-exposure is not necessary. Color films are considerably softer than black-and-white materials when wet and are more subject to physical damage until dry.

Contamination. In black-and-white negative processing, fixing-bath chemicals should not be allowed to contaminate the developer, because of the possible occurence of chemical fog that deteriorates the image being developed. In black-and-white reversal processing, contamination of one solution with another, such as the developer by the bleach solution, must be avoided, and water rinses should be used, as instructed, to avoid image deterioration and stains. In the much more complex color-processing systems, the water rinses between processing steps are very important because, when properly executed, they prevent contamination of the succeeding solution in the processing cycle. The rate of flow of water should be adjusted at least to provide good circulation around the film in the tank and thus present a continuous supply of fresh water at the emulsion surface. The temperature recommended is important primarily because residual chemicals in the emulsion layers are removed most efficiently at the specified temperature and the potential for physical damage to the emulsion at higher temperatures is avoided.

Some very serious effects occur when some solutions are contaminated. For example, if any of the hardening bath gets into the first developer, the reversal speed is lowered and the color balance may be shifted. A somewhat similar effect on the color balance will occur in Ektachrome processing if the color developer is contaminated with hardening solution. The addition of clearing bath to the color developer cannot be tolerated at all, and a serious shift in color balance may occur if the clearing-bath chemicals get into the bleach bath. These combinations are particularly serious and no tolerances are permissible. Contamination affects not only the characteristics of the image but also the useful life and the stability of the solutions concerned. It is obvious, therefore, that the processing instructions should be followed exactly in order to insure satisfactory results.

PHOTOGRAPHIC CONTROL

The processing instructions for a color product are the result of very careful testing by the manufacturer, and if followed in every detail, should render satisfactory color pictures, provided, of course, that the initial exposure was correct. However, in some cases, such as continuous processing, or in large-batch processing, it is important to know that the processing is under proper control and that consistently good results are being produced.

Consequently, the manufacturer often makes available correctly exposed but unprocessed test strips, along with a standard test strip exposed in the same manner and processed under standard conditions. The exposed strips are processed at selected intervals, and the results are compared with the check or standard test strip, either by visual examination or densitometric readings, or both. This comparison provides a direct check on the processing.

14

Washing Processed Photographic Materials

Water is used in photographic processing for removing chemicals from the emulsion following the various chemical treatments in order to avoid contamination of the following solutions. It is also used as a final wash to remove the chemicals of the final processing bath in order to avoid later damage to the image.

• The removal of processing chemicals from photographic materials has been of major interest for many years, and much has been learned about washing and the factors that are effective in an efficient operation. Although practically all washing studies have been made on the removal of residual fixing chemicals from black-and-white materials, many of the recommendations worked out can be applied to any of the washing operations in black-and-white or color processing. Since the general principles apply in all washing operations, many of the data obtained in these studies have been considered and incorporated in the processing instructions for color products.

Good washing of photographic negatives and prints is dependent upon the water supply, the design of the washing apparatus, and the manner in which the apparatus is used.

An understanding of the mechanism of washing is important in both the design and the successful operation of washing apparatus. Without discussing the mathematics of washing, it can be described as follows: Consider a layer of plain gelatin which has been coated on a sheet of glass or film base and treated in one of the various solutions — for instance, the fixing bath. The layer contains fixing-bath chemicals in solution dispersed throughout the gelatin. If it were possible to insert this sheet carefully into a tray of water without any agitation, a slight dilution of the hypo at the surface would occur, but, since the system is stagnant, the hypo would not be removed from the gelatin layer or its surface. Slight agitation by moving the tray would remove the diluted hypo from the gelatin surface and allow fresh water to take its place, so that the dilution of more hypo in the gelatin could occur. As this operation is repeated, more hypo is removed from deeper in the gelatin layer until finally all of the hypo is removed.

The hypo can be removed either by washing in a series of trays of water or in a single apparatus with running water. In the first case, the water rapidly becomes contaminated with hypo until the hypo solution in the tray reaches an equilibrium with the hypo in the emulsion layer. This means that the concentrations are such that no more hypo can diffuse out of the gelatin. The prints or negatives are then transferred to the next tray of fresh water, and the operation is repeated until the hypo has been removed.

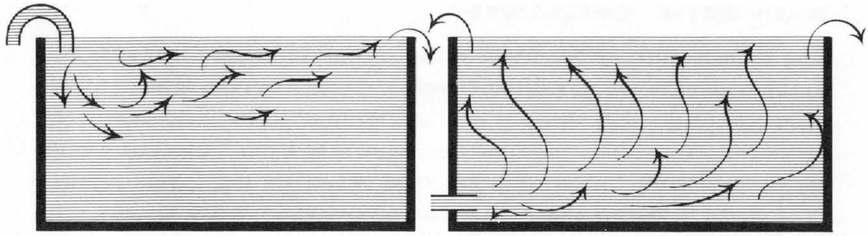
PHYSICAL FACTORS IN WASHING

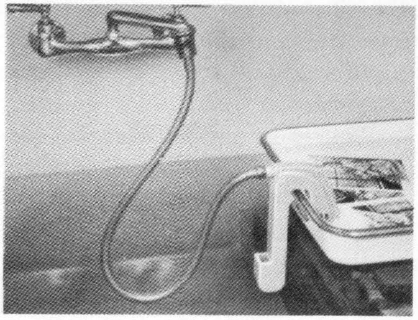
Running water is generally available today, and therefore most washing or rinsing is done in a single unit through which water flows under more or less controlled conditions. The efficiency of a washing system is dependent directly upon (1) the rate of flow of the water in gallons per minute, (2) the number of changes of water volume in the unit in a given interval of time, and (3) the design of the washing apparatus.

The first two of these factors are intimately tied together. In any simple washing apparatus, the flow of water should be adjusted to provide a complete change of the volume of water once in every five minutes. This condition can be readily established by adding ½ to 1 ounce of a deep-colored dye solution or a potassium permanganate solution to the washing tank and measuring the time required for the color to disappear. This should occur within five minutes if the flow of water is sufficient, but, because of design and limitations on water supply, etc, may not be possible in some equipment.

Efficient washing cannot be obtained when a "trickle" of water is used. For example, many photographers processing sheet film place the film hangers in a tank of water that is being fed by a hose over one edge of the tank. When the rate of water flow is inadequate, turbulence and water replacement occur only in the upper part of the tank, while the water in the lower portion is essentially stagnant. As a result, the upper part of the film sheet is washed more than the area near the bottom. However, if the inlet is located at a bottom corner of the tank and the rate of water flow is adequate, good turbulence is obtained throughout the water volume and fresh water reaches the entire emulsion surface almost continuously.

Poor washing is obtained when water is allowed to just trickle through a hose at one end of a tray. There is not sufficient water movement or turbulence to keep the films or prints separated, and





Above—For efficient circulation of wash water, the inlet should be located not at the top of the tank (left), but at a bottom corner (right).
Right—For efficient washing in a tray, a tray siphon is recommended.

washing is effective only at the edges. However, if a tray siphon or similar nozzle is used and the water flow is sufficient to provide a forceful jet of water, then efficient washing is obtained.

The size of the wash tank or tray is very important and should be selected according to the quantity and size of the films or prints to be processed. For example, one dozen 8 by 10-inch prints cannot be washed efficiently or adequately in an 8 by 10-inch tray because the prints cannot be separated and moved around adequately. They should be washed in a tray 16 by 20 inches or larger in size. Also, the depth of water should be adjusted to permit the prints to be moved freely. Any unnecessary depth of water is wasteful because a greater rate of flow is required to accomplish satisfactory washing in a minimum time.

When the washing tank is too large to permit the use of a tray siphon, then the design with respect to water inlets and drainage facilities is important. In a well-designed print washer, the inlets are arranged to provide maximum turbulence with a minimum of water and to prevent the accumulation of prints at the center. Submerged inlets at the bottom of the tank are very efficient when properly located. Overhead-spray washers provide adequate movement and turbulence but usually require a greater water flow and tend to splash. Several well-designed commercial units are available.

WASH-WATER TEMPERATURE

The temperature of the wash water has a very significant effect on the rate of removal of residual hypo and silver complexes from both films and prints. For many years the literature stated that high water temperatures actually retarded the removal of hypo. This is true when temperatures well above the practical range are employed, because the gelatin in the emulsion is swelled to an extent that interferes with the diffusion processes operating at normal processing temperatures. Investigations during more recent years have shown that water temperatures at 40 F and 80 F cause, respectively, slow and more rapid removal.

Figures 12 and 13 illustrate the relative effects of 40 F, 65 F, and 80 F temperatures. The data in both figures, obtained under carefully controlled conditions, indicate that more hypo is removed in a specified time as the water temperature is increased. In the case of film processing, the total time required to remove all of the hypo is decreased about 30 percent by raising the temperature from 40 to 80 F.

Because of the more complex structure of photographic prints, as stated before, there remain small amounts of hypo that cannot be removed by washing alone. The amount remaining is essentially the same for single- or double-weight paper if short fixing times are employed. When all of the physical characteristics of film and paper products are considered, it is concluded that *tempered water* should be used at 65 to 70 F to obtain the most efficient hypo removal.

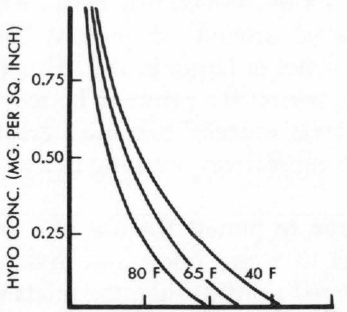


FIGURE 12. Film

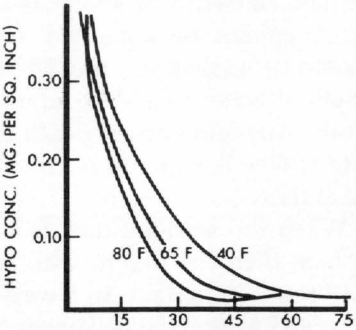


FIGURE 13. Paper

CHEMICAL FACTORS IN WASHING

Even with the most efficient equipment design and the optimum rate of water flow, adequate removal of chemicals from a photographic material generally requires an undesirably long time. Therefore, various chemical means have been sought for shortening the time needed, either by decomposing the undesired chemicals, or by speeding up the rate at which they can be removed.

For instance, in the photographic processes which include a number of separate chemical steps, such as reversal processing, it is desirable to have the rinses as short as possible, in order to avoid excessively long total processing times. Therefore, each chemical bath must be compounded so that it can tolerate a small quantity of the chemicals from the preceding bath and, if necessary, neutralize or decompose them so that they will not affect still later steps. Thus, in reversal processing, the clearing bath that is used after the bleach counteracts the oxidizing action of any bleach chemicals remaining in the emulsion and helps to remove the silver compounds formed by the bleaching of the negative image, and also conditions the remaining silver halides to respond to the re-exposure and second development.

Similarly, for shortening the time required for washing black-and-white prints, various compounds have been proposed for decomposing the hypo or converting it to some harmless compound. Unfortunately, most of these treatments have utilized acid oxidizing solutions which did not oxidize the hypo all the way to the harmless sulfate, but formed intermediate compounds, such as tetrathionate, which were just as bad as the hypo with respect to the fading action. Also, the solutions themselves frequently tended to attack the silver images, especially in the low-density areas.

In 1940, an effective alkaline oxidizing solution was recommended. This contained hydrogen peroxide and ammonium hydroxide in the correct proportions to produce a pH of 9.5 or higher and to oxidize the hypo completely to harmless sodium sulfate. This "hypo eliminator" was valuable for removing the last traces of hypo from prints which were to be kept for a long time, but it tended to complicate the washing procedure and did not greatly reduce the washing time.

More success, particularly in the latter respect, has been attained with treatments which speed up the rate of removal of the undesired chemicals.

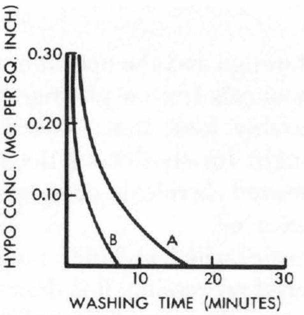


FIGURE 14. Non-hardening fixing bath
(A) at pH below 4.9
(B) at pH above 4.9

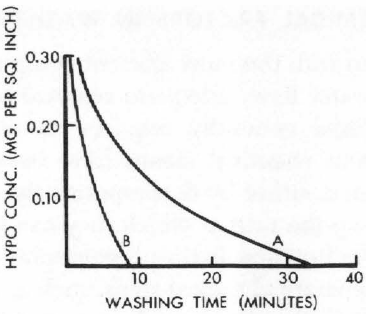


FIGURE 15. Acid-hardening fixing bath
(A) at pH below 4.9
(B) at pH above 4.9

THE pH EFFECT

On page 34 in Chapter V, the ionization of salts in solution was described as the division of some of the molecules into electrically charged atoms or groups of atoms called "ions." Hypo, or sodium thiosulfate, ionizes in solution in this manner:

$$Na_2S_2O_3 \longrightarrow 2\,Na^+ + S_2O_3^{--}$$

The gelatin used in the photographic emulsion is a colloid, as mentioned on page 18, and has some special properties. In its very complex structure are considerable numbers of amino ($—NH_2$) and carboxyl ($—COOH$) groups which are, respectively, alkaline and acid in nature. When a gelatin solution or a wet gelatin film coating is adjusted to a pH of about 4.9, the activity of these two types of groups is balanced and the gelatin is neutral with respect to acid or alkali. This pH value of 4.9 is called the "isoelectric point" of the gelatin. Of particular significance in the washing of emulsions is the fact that when the pH of the gelatin is lower than the value 4.9, i.e., more acid, the gelatin will adsorb the negatively charged thiosulfate ions ($S_2O_3^{=}$) from the fixing bath, but when the pH value is higher, i.e., more alkaline than the value 4.9 the gelatin will not adsorb the thiosulfate ion. The silver complexes formed in the fixer also ionize to produce negatively charged complex ions that adsorb to the gelatin when it is at a pH value below 4.9.

The practical significance of these effects is shown in Figures 14 and 15 which present the data obtained in carefully controlled experiments using a nonhardening fixing bath and a hardening fixing bath with the pH adjusted first to a value below 4.9 and then to a value above 4.9.

Even though acid hardening fixing baths, for various practical reasons, are used at pH values below 4.9, it is possible to make use of this pH effect by making the wash water sufficiently alkaline to bring the pH of the film emulsion quickly to a value above 4.9. This can be done by adding a small quantity of ammonia to the water.

This pH effect does not give as much advantage with paper prints as it does with films and plates, probably because the paper base plays an important part in the washing reactions.

WASHING WITH SEA WATER

The possibility of using sea water in locations where fresh-water supplies were scarce was of especial interest to the United States armed forces during World War II. It was found that both processed films and prints could be washed more rapidly in sea water, as shown in the figures below. In general, under similar washing conditions, the hypo could be removed from film in about one-third the normal time with fresh water and from prints in one-fifth to one-tenth the normal time.

Why sea water, which is essentially a 2.6 percent solution of sodium chloride, has this marked effect is not definitely known, but it is certainly connected with the salt content. Similar results were obtained when a 3.0 percent sodium chloride (purest-grade table salt) solution was substituted for sea water.

However, from a permanence viewpoint, any residual sodium chloride left in films or prints, especially in the presence of a small amount of hypo, increased the tendency of the image to fade. It is therefore

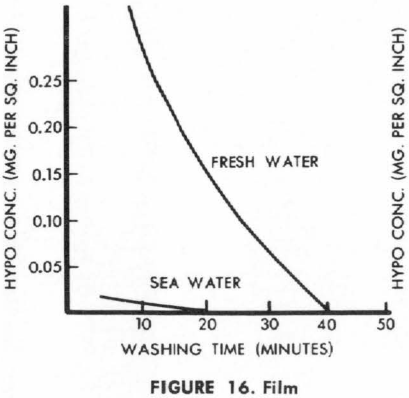


FIGURE 16. Film

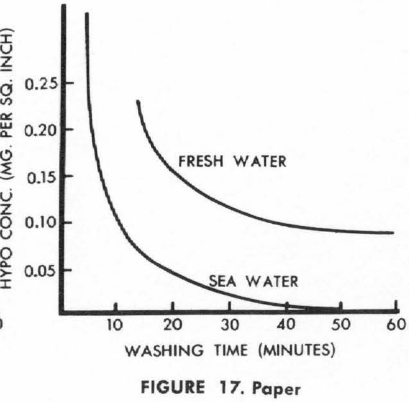


FIGURE 17. Paper

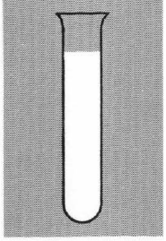
absolutely necessary to *remove the sea-water salts by using a final 2- to 5-minute wash in fresh water.* Although the effect is not so large, the action of Kodalk Balanced Alkali in print washing is probably quite similar to that of sea water or 3 percent salt solution.

WASHING AIDS

The results obtained with sea water and 3 percent sodium chloride solution indicated that a more satisfactory solution might be compounded with inorganic salts as effective as sodium chloride but harmless to the photographic image from a permanence viewpoint. Other salts were found that were nearly as effective. The term "washing aids" has been applied to this type of solution. Recently, there have been made available several proprietary products, such as BFI 30, G-E Hypo Neutralizer, and Kodak Hypo Clearing Agent, all having a similar action in the removal of residual hypo from films and prints.

These products have been successfully used in both batch and continuous processing systems for films and paper. However, the best method of application for each processing system must be worked out using control tests for residual hypo concentration to determine how effective the washing aid really is. When used efficiently, possible advantages include: (1) lower water consumption and cost; (2) increased production; (3) reduced labor costs; (4) lower priced negatives and prints to the consumer; and (5) less residual hypo in films and prints, with a consequent increase in their keeping life.

15



Practical Washing Requirements

The importance of thorough washing is often overlooked despite the fact that the need for it has been known ever since the first paper prints were made. Washing is an extremely important operation in the photographic process, and the effectiveness with which it is carried out has a direct effect on the keeping characteristics of negatives and prints.

• There is nothing more discouraging than to have prints which have been carefully mounted either on mounting board or in an album turn yellow or brown or to have a valuable industrial or research record lose important detail because of image fading.

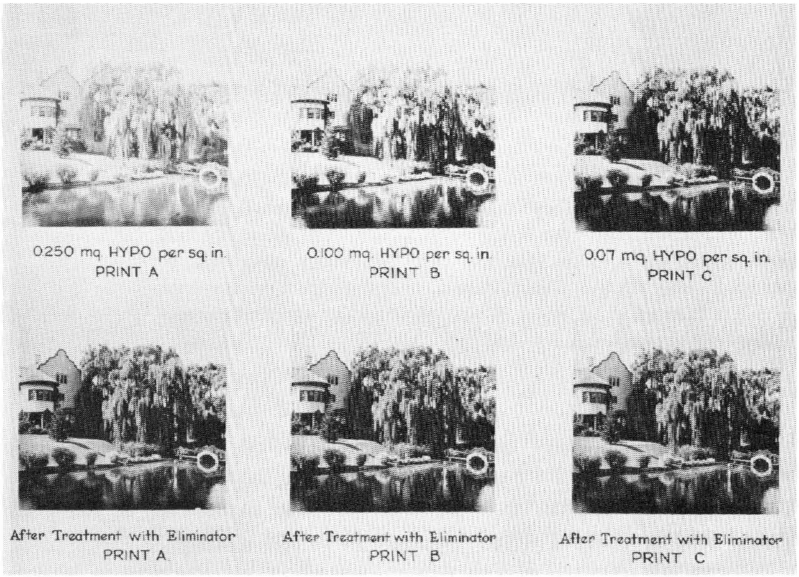
Why is the removal of fixing-bath chemicals by washing so important? If hypo is left in a black-and- white negative or print, a reaction can take place between the hypo and the silver image and produce yellowish-brown silver sulfide, a reaction similar to the tarnishing of silverware. Both effects are produced by the action of sulfur-containing compounds on metallic silver. In the tarnishing of silverware, hydrogen sulfide from cooking gas or coal gas, for example, acts on silver according to the reaction

$$\underset{\text{hydrogen sulfide}}{H_2S} + \underset{\text{silver}}{2\,Ag} = \underset{\text{silver sulfide}}{Ag_2S} + \underset{\text{hydrogen}}{H_2}$$

Similarly, hypo acts on the silver image in this manner:

$$\underset{\text{hypo}}{Na_2S_2O_3} + \underset{\text{silver}}{2\,Ag} = \underset{\text{silver sulfide}}{Ag_2S} + \underset{\text{sodium sulfite}}{Na_2SO_3}$$

the change in the tone or color of the image as a result of this reaction is called "*fading.*" Since most chemical reactions are accelerated by high temperatures, especially in the presence of moisture, elevated temperatures and high relative humidity speed up the sulfiding of the silver image. When sulfided images are exposed to these severe conditions for extended periods of time, especially when the amount of residual hypo is quite high, the silver sulfide can be oxidized slowly to silver sulfate which is both white and soluble. When this occurs,



Fading caused by hypo which was not removed in washing. The bottom prints demonstrate the results obtained with a hypo eliminator (Hypo Eliminator HE-1).

the image actually begins to disappear, first in the lowest density areas, and cannot be recovered.

If complex silver compounds are left in the processed negative or print, they can also produce silver sulfide, especially under conditions of high temperature and humidity. In this case, the yellowish-brown stain of silver sulfide is the result of a decomposition, or breakdown, of the complex compounds which contain both silver and hypo, and the discoloration can be formed over the entire area of the negative or print and not in the image areas only. Therefore, as a result of a relatively small amount of the complex compounds, an undesirable stain can appear on photographic prints.

In the case of color images, proper washing is equally important. Even though the images are composed of dyes rather than silver, they also are subject to attack by hypo or other processing chemicals left in the emulsion. Since three different dyes are involved in each case, the effects caused by any particular chemicals left in the emulsion can be quite complicated, and are therefore much harder to predict. And since the image color can be noticeably affected by even slight changes in the proportions of the dyes, any action by the residual chemicals is likely to have a serious effect on the image quality.

Thus, in any color processing it is important to provide efficient washing, as discussed in the preceding chapter, and to follow the processing instructions closely. Because compositions of the final baths and the subsequent washing requirements differ so considerably in the various color processes, it is not practical to attempt to consider them in detail here. Therefore, the discussion in the remainder of this chapter will deal only with the washing requirements and some of the factors affecting the washing of black-and-white silver images after the usual fixing operation.

Photographic films and paper prints are discussed separately because of the differences in the structures of the two type of products. Films consist of an emulsion layer coated on a film base which does not absorb processing solutions. Photographic printing papers consist of three layers — paper stock, baryta coating, and emulsion, all of which absorb and retain fixing-bath chemicals. Similarly, photographic paper for photocopy and drawing-reproduction applications consist of the paper stock and the emulsion coating. One exception is waterproof paper which behaves essentially in the same manner as film products because the emulsion is coated on a water-resistant paper.

Film Processing. It is general practice to use acid hardening fixing baths in the processing of photographic films, because the emulsions cannot be hardened in manufacture to a degree sufficient to permit satisfactory handling under the many processing conditions that may be employed by the consumer. However, in some cases, advantage can be taken of nonhardening fixing baths or special acid hardening fixers.

When a potassium alum hardener is used in the fixing bath, the washing time is increased considerably over that required after a nonhardening bath, but the effect of the pH of the bath still holds, as shown in Figures 14 and 15. Chrome alum hardeners do not produce an increase in the washing time, but ordinarily this does not offer enough of an advantage to offset the practical difficulties in the use and control of chrome alum fixing baths.

Since the processing chemicals are not absorbed by the film base, the washing operation has only to remove the chemicals from the emulsion layer. This is a comparatively straightforward and uncomplicated operation, requiring only an adequate water supply and suitable equipment to hold the film.

Print Processing. Photographic prints are more difficult to wash than films, primarily because the amounts of residual hypo retained in the paper support and the baryta coating far exceed the quantities held by the relatively thin emulsion coatings. This has been confirmed by photomicrographic examination of cross sections of processed prints treated in silver nitrate solution to convert the hypo to brownish-colored silver sulfide.

There is a very significant relationship between the time of fixation and the washing of photographic prints. It has been found that fixing times in excess of the currently recommended 5 to 10 minutes permit the diffusion of hypo into the internal structure of the paper fibers as well as into the spaces between the fibers. Hypo within the fiber structure is extremely difficult to remove by washing. This was confirmed in practical washing tests with both single- and double-weight papers which had been fixed for excessively long times. These showed, on analysis, that the double-weight prints contained approximately twice as much residual hypo as single-weight prints, even after 48 hours' washing. On the other hand, when the recommended fixing times were used, both double- and single-weight prints were washed to the same residual hypo concentration in the same length of time. Therefore, from the viewpoint of maximum permanence and minimum production time, it is important to fix photographic prints as recommended, that is, for 5 to 10 minutes, no longer.

WASH-WATER SUPPLY

The condition of the water with respect to its chemical composition and any contamination can affect the photographic material washed in it. The fact that some perfectly clear water is called "hard water" is familiar to nearly everyone. It is hard because salts of calcium and magnesium are dissolved in it as a result of the flow of the water through or over certain kinds of soil and rock structures. The scale found in steam boilers or kettles is formed by the deposition of these salts from hard water. Hard water does not have any bad effects and can be used without endangering the permanence of negatives and prints.

However, hard water is sometimes contaminated by mineral sediment or by rust particles from iron pipes. Such particles should be removed from the water by using a suitable filter. Rust can stick to the photographic emulsion, producing brown specks on prints and negatives and either spoiling the print appearance or forming opaque spots on negatives which cause white spots on prints made from such negatives. Mineral particles, like sand, may stick to negatives and produce scratches when attempts are made to remove them. This is serious in commercial and professional negatives and especially in small-size negatives, such as those exposed in miniature cameras, which are enlarged in printing.

In some areas, such as volcanic regions, the water may contain dissolved sulfides. These are best removed by boiling the water and thus causing the sulfides to leave the water in the form of hydrogen sulfide gas. It is important to remove these compounds because they could affect the silver image if left in negatives or prints. Sometimes, when water is obtained from swamp and marsh areas, it is colored because of dissolved colored substances from decayed vegetation. These can also be removed by boiling and filtration.

Generally, it is reasonable to assume that a water supply is satisfactory for photographic washing if it is clear, is clean, is free from rust or mineral particles, and does not have a sulfide odor on heating. Even sea water can be used, as was discussed in the preceding chapter.

CONTROL TESTS FOR WASHING

To determine the efficiency of washing of processed photographic materials, it is necessary to employ tests that indicate the amount of residual hypo and silver remaining *in the negative or print.* Many tests have been recommended in the photographic literature. Most have been based on chemical reactions between various reagents and the drippings collected from negatives or prints, or on electrical measurements of the wash water. These methods are inaccurate because they do not take into account hypo and silver salts retained in the photographic material. This is particularly true in the case of photographic prints which consist of a paper support, an emulsion layer, and a baryta coating. All three layers are capable of holding hypo that is difficult to remove and certainly will not diffuse out of the print by dripping. Extensive research has confirmed these facts and shown that the determination of residual hypo and silver must be made on samples of the negative or print.

Tests for Photographic Prints. In 1943, Crabtree, Eaton, and Muehler described a quantitative test for the estimation of hypo in prints. An unexposed sheet of paper, of the same size and kind as the batch being processed, is carried through the processing cycle and, after washing, is immersed in an acidified solution of silver nitrate, which reacts with hypo to form a yellowish-brown stain of silver sulfide (Ag_2S). The excess silver nitrate is removed by treating the print in sodium chloride to convert the silver salt to the halide, silver chloride, which is then dissolved out in a hypo solution. This procedure is necessary in order to remove the excess silver nitrate which would darken in light and provide a false analysis.

The transmission densities of the paper before and after treatment with silver nitrate are read on a densitometer fitted with a Kodak Wratten Filter No. 44 (blue-green). The difference in the readings corresponds to the density of the silver sulfide which, in turn, is proportional to the residual hypo that was present in the print. The amount of hypo is determined by reading a standard curve showing the relationship between density and hypo concentration. The method is quantitative and should be used for the accurate determination of residual hypo.

Because this complete procedure is not convenient to use in many production operations in studios and laboratories, a spot-test adaptation of it has been recommended for approximate or qualitative estimation. It involves the application of a spot of acidified silver nitrate solution to the unwanted edge of the face of either a dry or wet processed print or to an unexposed print included for the purpose. After the approximately 2 to 3 minutes required for the reaction to be completed, the stain is compared with a series of calibrated printed stains. The Kodak Hypo Estimator is useful for this purpose.

Tests for Photographic Films. In 1930, Crabtree and Ross described a quantitative method for the estimation of residual hypo in film samples. It is based on the comparison of the turbidity formed in a test solution with the turbidities produced by known quantities of hypo. In use, 10-cc volumes of the test solution containing mercuric chloride and potassium bromide are added to each of a series of test tubes. Increasing amounts of a solution containing a prescribed amount of hypo are then added to all of the tubes but two. A one-inch square of the processed film is then folded and placed in one of the two remaining tubes. Almost immediately a white compound is formed that makes the solutions turbid or cloudy. After about five minutes with occasional agitation, the turbidity in the film-sample tube is compared with each of the other tubes to find the one it most nearly matches. The quantity of residual hypo in the film is the same as the quantity of hypo added to the matching tube. This method is capable of measuring hypo concentrations less than 0.005 milligram per square inch. The method was adopted by the National Bureau of Standards, Washington, D. C., as the standard procedure for the estimation of hypo in the preparation of permanent film records, and it was specified that such records should contain not more than 0.005

milligram per square inch.

Although this method is quantitative, it is time-consuming and difficult to use as a routine control test in commercial processing operations. Consequently, a spot test with the silver nitrate-acetic acid solution described earlier has been adapted to the estimation of hypo in film samples. To make a test, a drop of the test solution is placed on a clear area at the edge of the film, allowed to stand for 2 or 3 minutes, and rinsed off. The strength of the stain produced in the test spot provides a good indication of the amount of hypo left in the film. A fairly precise quantitative estimate can be made by comparing the spot with the standard color patches on the Kodak Hypo Estimator. These color patches were printed on cellulose acetate sheet with printing inks selected to match the stains produced by the test on films having various known quantities of hypo.

Test for Residual Silver. When fixing baths are used until the concentration of silver complexes in the solution is quite high, both photographic films and papers tend to retain some of these compounds even after prolonged and thorough washing. As stated before, these silver complexes can decompose to produce a yellowish silver sulfide stain over the whole area of the negative or print. It is particularly noticeable on prints because of the white background. The actual quantity of silver complexes required to produce this effect is quite small, and no simple quantitative method has been evolved for its estimation. However, the stain that might be produced, especially under conditions of high humidity and temperature, can be simulated by means of a simple drop test. This consists in placing a drop of very dilute sodium sulfide solution (0.2 percent) on a nonimage area of a squeegeed or dried film or print and observing after about one minute whether or not any stain is formed. The excess test solution should be removed with a blotter before the test area is observed. Obviously, if the films or prints are properly fixed in the first place, a negative test will be obtained. Any light-yellow or cream-colored stain, however, indicates the presence of residual silver. This residual silver should be removed by refixing in a fresh fixing bath and washing.

WASHING REQUIREMENTS IN PRACTICE

Some of the important factors in the washing of photographic materials have been discussed. These are important in any studio or laboratory production where efficient processing is concerned. "How far is it necessary to go with respect to washing?" is a logical question at this point. The answer, of course, depends on the use to which the photographic image will be put. For example, in many technical fields the photographic record is used and discarded very shortly after it is obtained. In these cases, it is not necessary to remove all of the residual hypo and silver. On the other hand, the photofinisher, the portrait photographer, the motion-picture producer, and many others are interested in the production of a photographic record that can be kept for a long time by the consumer. Each case or application should be considered seriously with respect to the desired permanence of the photographic record, and the processing should then be planned accordingly. Where there is any doubt, all practical precautions should be taken to produce the most permanent records.

If long life of the photographic record is not required, it is not necessary to reduce the silver and hypo to the absolute minimum. Therefore, in practice, there are two requirements, namely: (1) "commercial" washing for materials with an expected keeping life of a few decades or less, and (2) "archival" washing wihch implies removal of all substances which might affect either the image or nonimage areas during long-time storage. It is difficult, if not impossible, to state specific concentrations of residual hypo that can be tolerated in all cases. However, on the basis of experience in temperate climates, together with accelerated fading tests at 110 F and 100 percent relative humidity, suggested maximum permissible hypo concentrations have been proposed for some general classes of photographic films and prints.

SUGGESTED MAXIMUM PERMISSIBLE CONCENTRATION OF HYPO

Films	***Commercial Use (mg per sq inch)***	***Archival Use (mg per sq inch)***
Fine-grain motion-picture positive films	0.02	0.005
Coarse-grain motion-picture negative films	0.20	0.005
Amateur & professional films	0.15 —0.25	0.005
X-ray films	0.25 —0.50	0.005
Fine-grain x-ray films	0.15 —0.25	0.005
Prints		
Double-weight	0.10 —0.15	Nil.
Single-weight	0.05 —0.10	Nil.

In general, the differences in the suggested maximum permissible concentrations of hypo for different films depend on the fact that fine-grain emulsions fade more rapidly under accelerated fading conditions than the coarse-grain emulsions. The residual quantities indicated for amateur, professional, and x-ray films are higher because these types fade more slowly, as in the case of x-ray films, or the image-keeping requirements are not as stringent, as with the amateur and professional films.

Whether or not these suggested residual hypo concentrations are too high depends on the conditions of storage or keeping, with regard especially to the relative humidity and temperature. For example, photographic prints containing 0.10 milligram of hypo per square inch have been stored without damage for years in file drawers in temperate climates, but similiar prints fade quite rapidly under tropical conditions. It is, then, important to wash more thoroughly in the tropics to improve the permanence and, perhaps, to consider the use of suitable hypo eliminators for the removal of the last traces of hypo.

In concluding this discussion, certain important factors in the storage of negatives and prints should be mentioned. Many negative storage envelopes are made of kraft paper and have a center seam. In many types, a cement or adhesive that will absorb moisture from the atmosphere is used. This produces a condition, equivalent for all practical purposes, to a high relative humidity. If the negatives contain residual hypo and silver, fading can occur in areas corresponding to the envelope seam. Therefore, envelopes designed with a side seam should be used; and they should be put together with a nonhygroscopic adhesive. Specifications for negative-storage envelopes have been outlined in American Standard Z38.8.21.

Similarly, photographic prints should be mounted in albums with cements or adhesives that do not absorb moisture and do not contain sulfur. Both moisture and sulfur can cause localized fading. The preferred mounting technique is to use a dry-mounting tissue.

APPENDIX

1

Principles of Color Processes

Compared to black-and-white films, the sensitized materials used in three-color photography are complex. The basic principles of color photography are common to most of the current color processes.

• The principles of three-color photography have been described in detail in many treatises. However, a brief outline of these principles should serve to emphasize the complexities in color processing that do not exist in black-and-white photography, whether the process is based on negative-positive or reversal processing. It is helpful to understand the structure of color materials and to know how color processing is related to the exposure of the film.

It was pointed out in Chapter IV that the visible spectrum can be divided into three color regions – blue, green, and red – by the use of blue, green, and red filters, respectively. Each filter transmits its own color and absorbs the remaining colors. Similarly, when a colored object, illuminated with white light, is photographed on black-and-white film through a filter placed on the camera lens, the filter transmits its own color and absorbs the remaining colors. If the filter is blue, the film records the blue color of the object (Figure 18), but none of the other colors of that object. Therefore, with panchromatic-sensitized silver halide emulsions and the three color-separation filters, it is possible to obtain separate camera-film records of the blue, green, and red color components of an object. These are records of the *primary* colors of the object.

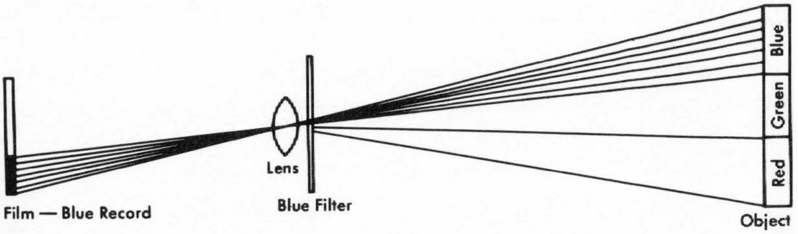


FIGURE 18

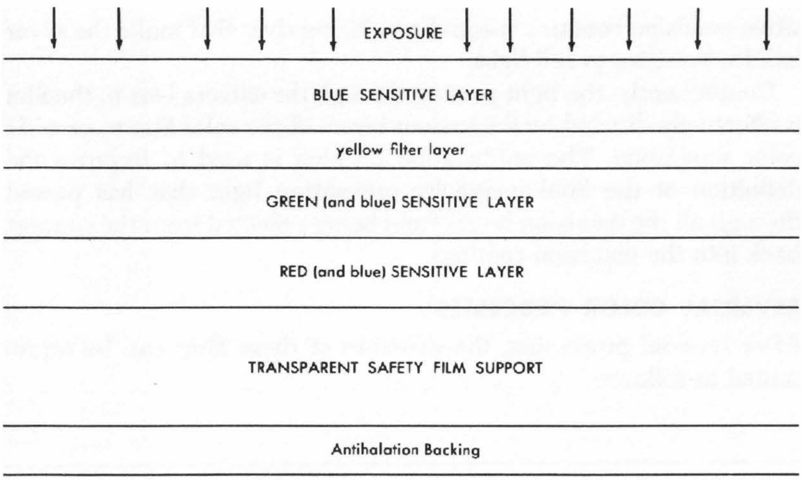


FIGURE 19 The structure of color film

In practical photography, it is impossible to make three color separations – one on each of three sheets of film – of moving or changing subjects unless quite complex and expensive camera equipment is employed. Even so, the three black-and-white separation records must then be converted into a color print, which requires considerable equipment, time, and experience. Fortunately, it has been possible to manufacture special color films that can record the separate colors simultaneously and then be processed to provide the final transparency. These products are known as *integral tripack color films,* examples of which are Kodachrome Film, Kodak Ektachrome Film, and Kodak Ektacolor Film.

Figure 19 illustrates the physical structure of this type of color film. During exposure the light strikes the blue-sensitive layer first, and a record of the blue component of the object is obtained. This emulsion is sensitive to blue light only and does not respond to green or red. Therefore, only a blue record is obtained. However, the silver halides in all of the emulsion layers are sensitive to blue light, and in order to prevent the formation of a blue record in the two bottom layers, a yellow filter layer formed from finely divided silver, known as "Carey-Lea silver," is coated just under the blue-sensitive layer to absorb all of the blue from the light passing through it.

The green-sensitive emulsion contains spectral sensitizing dyes that make the silver halides sensitive to green light but not to red light which is transmitted through this layer to the next one. The red-sensitive emulsion contains spectral sensitizing dyes that make the silver halides sensitive to red light.

Consequently, the light passing through the camera lens to the film is effectively divided by the various layers of the color film to provide color separation. The antihalation backing is used to improve the definition of the final image by preventing light that has passed through all the emulsion layers from being reflected from the support back into the emulsion coatings.

REVERSAL COLOR PROCESSES

After reversal processing, the structure of these films can be represented as follows:

YELLOW dye — blue absorbing

MAGENTA dye — green absorbing

CYAN dye — red absorbing

Transparent Safety Film Support

Clear

FIGURE 20 Processed color film

Why are yellow, magenta, and cyan dyes formed during processing?

Two important facts should be remembered in order to understand these color processes: (1) the original exposure provided records of the blue, green, and red components of the colored object, and (2) the final color transparency or print is viewed in white light and, to look like the original subject, should permit just the right amount of blue, green, and red colors to reach the eye. This control is obtained by forming during processing the complementary colors of blue, green, and red — yellow, magenta, and cyan, respectively. Thus, the yellow absorbs blue in those areas where the subject did not reflect blue, the magenta absorbs green where there was no green, and the cyan absorbs red where there was no red.

NEGATIVE-POSITIVE COLOR PROCESSES

Color processes such as Kodacolor, Kodak Ektacolor, and Eastman Negative-Positive are also integral tripack color processes based on the same principles of three-color photography. After exposure, the films are processed to give color negatives composed of the complementary colors, yellow, magenta, and cyan. The color negatives are then used to expose either paper or film coated with essentially the same emulsion as the negative film. A processing cycle similar to that used for the color negative is employed to produce a positive color print or transparency image composed of the complementary colors.

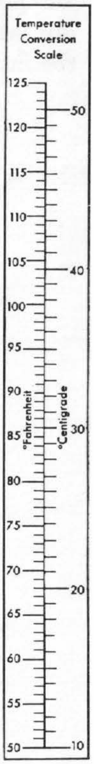
Therefore, the complementary dyes formed in both the negative and positive have controlled the absorption of the primary colors during viewing or projection and, if the original exposure was correct, the final color positive will look like the original.

APPENDIX

2

Weights and Measures Conversion Tables

In American photographic practice, solids are weighed by either the Avoirdupois or the Metric system and liquids are measured correspondingly by U. S. Liquid or Metric measure. The following tables give all the equivalent values required for converting photographic formulas from one system to the other:



Avoirdupois to Metric Weight

Pounds	Ounces	Grains	Grams	Kilograms
1	16	7000	453.6	0.4536
0.0625	1	437.5	28.35	0.02835
		1	0.0648	
	0.03527	15.43	1	0.001
2.205	35.27	15430	1000	1

U. S. Liquid to Metric Measure

Gallons	Quarts	Ounces (Fluid)	Drams (Fluid)	Cubic Centimeters	Liters
1	4	128	1024	3785	3.785
0.25	1	32	256	946.3	0.9463
		1	8	29.57	0.02957
		0.125	1(60 mins.)	3.697	0.003697
		0.03381	0.2705	1	0.001
0.2642	1.057	33.81	270.5	1000	1

Conversion Factors

Grains per 32 fluid oz multiplied by 0.06847 =grams per liter
Ounces per 32 fluid oz multiplied by 29.96 =grams per liter
Pounds per 32 fluid oz multiplied by 479.3 =grams per liter

Grams per liter multiplied by 14.60 =grains per 32 fluid oz
Grams per liter multiplied by 0.03338 =ounces per 32 fluid oz
Grams per liter multiplied by 0.002086 =pounds per 32 fluid oz

Grams per liter approximately equals ounces per 30 quarts
Grams per liter approximately equals pounds per 120 gallons
Ounces (fluid) per 32 oz multiplied by 31.25 =cubic centimeters per liter
Cubic centimeters per liter multiplied by 0.032 =ounces (fluid) per 32 oz
cm × .3937 =inches inches × 2.5400 =cm

APPENDIX

3

Partial Table of Elements

Name	*Symbol*	*Atomic Wgt.*	*Atomic No.*
Actinium	Ac	227	89
Aluminum	Al	26.98	13
Antimony	Sb	121.76	51
Argon	A	39.944	18
Arsenic	As	74.91	33
Barium	Ba	137.36	56
Beryllium	Be	9.013	4
Bismuth	Bi	209	83
Boron	B	10.82	5
Bromine	Br	79.916	35
Cadmium	Cd	112.41	48
Calcium	Ca	40.08	20
Carbon	C	12.011	6
Cesium	Cs	132.91	55
Chlorine	Cl	35.457	17
Chromium	Cr	52.01	24
Cobalt	Co	58.94	27
Copper	Cu	63.54	29
Fluorine	F	19	9
Gallium	Ga	69.72	31
Germanium	Ge	72.6	32
Gold	Au	197	79
Hafnium	Hf	178.58	72
Helium	He	4.003	2
Hydrogen	H	1.008	1
Indium	In	114.82	49
Iodine	I	126.91	53
Iridium	Ir	192.2	77
Iron	Fe	55.85	26
Krypton	Kr	83.8	36
Lead	Pb	207.21	82
Lithium	Li	6.94	3
Magnesium	Mg	24.32	12
Manganese	Mn	54.94	25
Mercury	Hg	200.61	80
Molybdenum	Mo	95.95	42
Neon	Ne	20.183	10
Nickel	Ni	58.71	28
Niobium	Nb	92.91	41
Nitrogen	N	14.008	7
Osmium	Os	190.2	76
Oxygen	O	16	8
Palladium	Pd	106.7	46
Phosphorus	P	30.975	15
Platinum	Pt	195.09	78
Polonium	Po	210	84
Potassium	K	39.1	19
Radium	Ra	226.05	88
Radon	Rn	222	86
Rhenium	Re	186.22	75
Rhodium	Rh	102.91	45
Rubidium	Rb	85.48	37
Ruthenium	Ru	101.1	44
Scandium	Sc	44.96	21
Selenium	Se	78.96	34
Silicon	Si	28.09	14
Silver	Ag	107.88	47
Sodium	Na	22.991	11
Strontium	Sr	87.63	38
Sulfur	S	32.066	16
Tantalum	Ta	180.95	73
Tellurium	Te	127.61	52
Thallium	Tl	204.39	81
Thorium	Th	232.05	90
Tin	Sn	118.7	50
Titanium	Ti	47.9	22
Tungsten	W	183.86	74
Uranium	U	238.07	92
Vanadium	V	50.95	23
Xenon	Xe	131.3	54
Yttrium	Y	88.92	39
Zinc	Zn	65.38	30
Zirconium	Zr	91.22	40

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ABOUT THE AUTHOR

George T. Eaton, Head, Photographic Chemistry Department and Assistant Division Head of the Applied Photography Division at Kodak Research Laboratories. He has been associated with the Eastman Kodak Company since 1937. He worked as a research chemist, supervisor of the industrial sales laboratory, technical editor, and other projects.

The Photographic Society of America awarded Mr. Eaton an associateship in 1945 and a fellowship in 1952. He is also a fellow and former president of the Society of Photographic Scientists and Engineers.

For nine years he taught photographic chemistry for evening classes at the Rochester Institute of Technology. In addition to these many activities Mr. Eaton has found time to write numerous scientific papers related to photographic chemistry.

MORGAN & MORGAN, Inc., Publishers
Hastings-on-Hudson, N.Y. 10706
Fountain Press, London

EATON

PHOTOGRAPHIC CHEMISTRY

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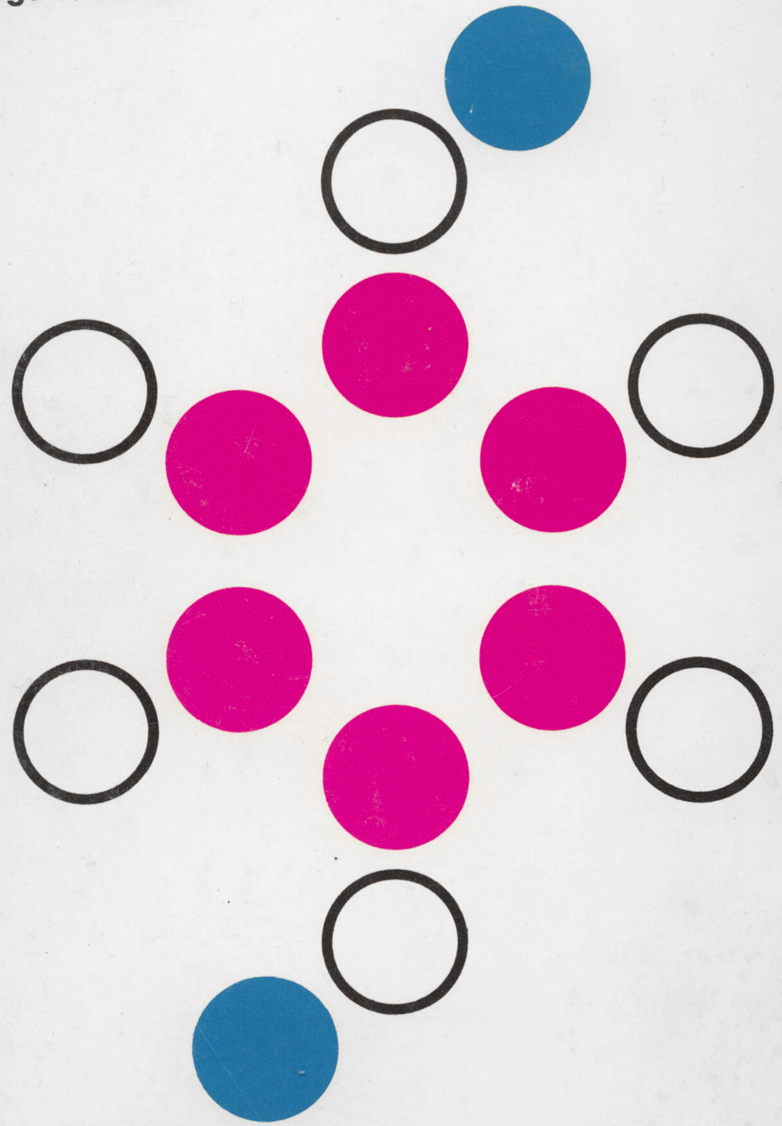
Photographic Chemistry

IN BLACK-AND-WHITE AND COLOR PHOTOGRAPHY

by George T. Eaton



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by George T. Eaton

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This book is intended primarily for those who are active in photography or the photographic industry, who have had very little or no formal training in chemistry, physics or photographic theory. It is written for the purpose of giving these people a better understanding of the photographic process and, therefore, of the operations they are required to carry out in their everyday work.

A basic knowledge and understanding of photographic processing is one of the most important requisites in this new trend since all photographic material must be processed and since users of photographic materials are becoming more and more conscious of the importance of correct processing to insure better results, greater permanence, and more economical operation.

It should be of interest to the layman, to the amateur and professional photographer, to the industrial photographer, to the production people in the photographic industry and even to those trained scientists working in other branches of the photographic science. The book might be used as a text in high schools, in evening schools and extension courses designed to provide, on an elementary level, a better understanding of the photographic process.

The 15 chapters and additional reference pages include:
1. The Photographic Process. 2. Chemical History. 3. The Photographic Emulsion. 4. The Reaction of Photographic Emulsions to Light. 5. Solutions and Chemicals. 6. Developers. 7. Chemistry of Development. 8. Chemistry of Color Development. 9. Measurement of Development. 10. Control of Development. 11. Fixing Baths. 12. Reversal Processing. 13. Practical Color Processes. 14. Washing. 15. Practical Washing Requirements. 16. Principles of Color Processes. 17. Weights and Measures, Conversion Tables. Partial Table of Elements. Index.

MORGAN & MORGAN, Inc., Publishers
Hastings-on-Hudson, N.Y. 10706
Fountain Press, London

$4.95