

CHEMISTRY OF PHOTOGRAPHY

While it is easy to make comparisons between the pupil of the eye and the f-stop of a camera or between the retina of the eye and photographic film, once we get past the basic similarities of the optics of the two systems comparisons begin to rapidly break down. The eye is not only much more complex than a camera and its film, but the two imaging devices function by chemically different mechanisms. The photographer (or the automatic exposure system of the camera) regulates the f-stop opening and time of exposure of her camera to match the sensitivity of film, while the iris and retina sensitivity of the eye adjust to correspond to the light level of the scene.

While science is slowly putting together the pieces to explain the functioning of our vision system, the basic nuts and bolts of classical photography have been known for years, although certain details remain the subject of some discussion. Just as in the human eye, classical photographic systems are composed of two separate, but interrelated processes – the basic black and white image structure and the finer points of color reproduction.

This first installment on the chemistry of photography is intended to introduce in a simplified way the basic concepts of silver halide photography. It will not delve into the physics of optics, the functioning of cameras and lenses, photographic techniques, non-silver processes, or the artistic aspects of photography. Nor will it go beyond a cursory mention of color photographic processes, which will be left for the future. Anyone interested in more detail is referred to the selected bibliographic material cited at the end.

A Brief History of Black and White Silver Halide Photography

Perhaps the earliest reference to the concept of silver-based black and white photography is that of J. H. Schulze who observed in 1727 that a mixture of silver nitrate and chalk darkened on exposure to light. The first more or less permanent images were obtained in 1824 by Nicéphore Niepce, a French physicist, using glass plates coated with a dispersion of silver salts in bitumen (a coal derivative). In the early 1830's, Niepce's partner, Louis Daguerre, discovered by accident that mercury vapor was capable of developing an image on a silver-plated copper sheet that had been previously sensitized by iodine vapor. The image, which was called a daguerreotype, could be made permanent by washing the plate with hot concentrated salt solution. In 1839 Daguerre demonstrated his photographic process to the Academy of Sciences in Paris. The process was later improved by using sodium thiosulfate to wash off the unexposed silver salts.

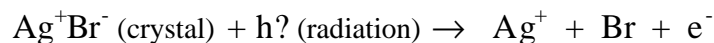
In 1841, an Englishman, William Henry Fox Talbot introduced a new system, the calotype process. The Talbot process involved a paper that had been sensitized to light by a coating of silver iodide. A negative image was produced on the exposed light-sensitive paper by bathing it in a solution of gallic acid in a development process essentially the same as that used today. If the paper base employed was semitransparent, the original negative image could be laid over another piece of sensitized paper which, when exposed and developed, yielded a "positive," or direct copy of the original. The process would be equivalent to what is termed "contact printing" today. Although the calotype process required less time than that of Daguerre, the Talbot images were not particularly sharp because of the fluidity of the medium employed to suspend the silver iodide crystals.

Originally, the silver salts were held on glass using egg white as a binder. This provided relatively sharp images although they were easily damaged. By 1871, the problem had been solved by Dr. R. L. Maddox, an amateur photographer and physician, who discovered a way to prepare gelatin dispersions of silver salts on glass plates. In 1887 George Eastman introduced the Kodak system in which a silver halide-in-gelatin dispersion was coated on a cellulose nitrate base and loaded into a camera. The camera could take 100 pictures and when all were exposed, camera and film were returned to Rochester, New York, for processing. With those innovations the age of modern photography had arrived.

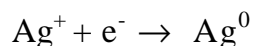
Photochemistry of Silver Salts

To understand the fundamental chemistry of silver-based photography, we must look at the photochemistry of silver salts. A typical photographic film contains tiny crystals of very slightly soluble silver halide salts such as silver bromide (AgBr) commonly referred to as “grains.” The grains are suspended in a gelatin matrix and the resulting gelatin dispersion, incorrectly (from a physical chemistry standpoint), but traditionally referred to as an “emulsion,” is melted and applied as a thin coating on a polymer base or, as in older applications, on a glass plate.

Figure 1 shows a schematic representation of the silver halide process. When light or radiation of appropriate wavelength strikes one of the silver halide crystals, a series of reactions begins that produces a small amount of free silver in the grain. Initially, a free bromine atom is produced when the bromide ion absorbs the photon of light:



The silver ion can then combine with the electron to produce a silver atom.



Association within the grains produces species such as Ag_2^+ , Ag_2^0 , Ag_3^+ , Ag_3^0 , Ag_4^+ , and Ag_4^0 . The free silver produced in the exposed silver halide grains constitutes what is referred to as the “latent image,” which is later amplified by the development process.

The grains containing the free silver in the form of Ag_i^0 are readily reduced by chemicals referred to as “developers” forming relatively large amounts of free silver; that deposit of free silver produces a dark area in that section of the film. The developer under the same conditions does not significantly affect the unexposed grains.

The radiation or light sensitivity of a silver halide film (referred to in the trade as its “speed” and denoted on commercial film as its ASA in the United States or DIN in Europe) is related to the size of the grain and to the specific halide composition employed. In general, as the grain size in the emulsion increases, the effective light sensitivity of the film increases - up to a point. An optimum value of grain size for a given sensitivity is found to exist because the same number of silver atoms are needed to initiate reduction of the entire grain by the developer despite the grain size, so that producing larger grains reaches a point of diminishing returns and no further benefit is obtained.

All photographic emulsions contain crystals of varying sizes, but within a given emulsion the range is from less than 0.1 micron in slow emulsions (e.g., for paper prints) to a few microns in “fast” negative emulsions.

An interesting modern innovation in photographic emulsion technology is related to the basic concept of silver halide grain geometry. In a classical silver halide crystal, typically a

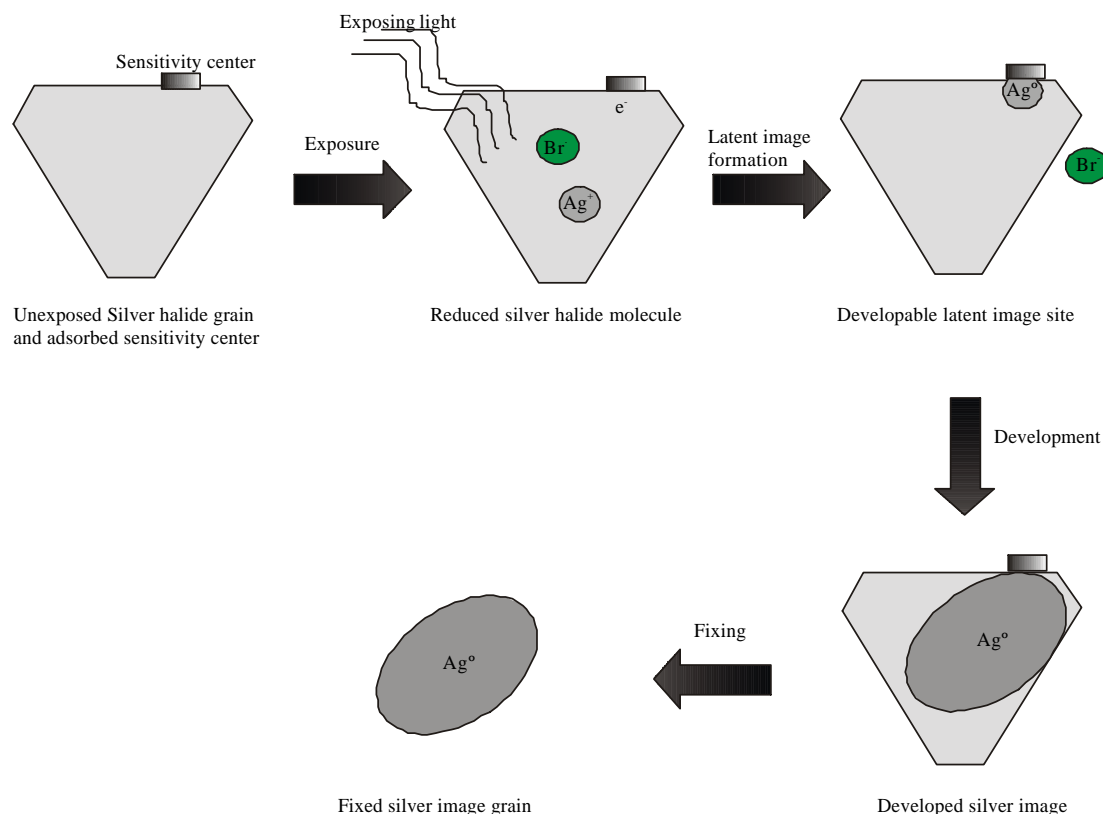


Figure 1: A simplified schematic representation of the silver halide process.

cubic crystal lattice, the structure will be relatively symmetrical in that the orientation of the crystal in the coated film will always present the same approximate surface area to be exposed. Extensive research efforts led to the development of grain precipitation processes that produced flatter “tablet” grains in which the crystals possessed a more asymmetric geometry, and in which a larger surface area was presented for exposure for the same given weight of silver halide (Fig. 2). That development resulted in significant improvements in film sensitivity and reductions in the amount of silver needed to obtain a given sensitivity – and a potentially important reduction in the cost of the film.

The Latent Image and Image Development

The silver halide process is by far the most important of all of the radiation-sensitive photographic systems in use today. The principal reason for this superiority is the high sensitivity of the system - the amount of radiant energy required to produce a useful image - and the extreme flexibility of the system in terms of adjusting sensitivity, contrast, tonal range and other such aspects of the product. The impact of a single photon on a silver halide grain, for example, produces a nucleus of at least four silver atoms, and that effect can be amplified as much as a billion times by the action of a properly chosen reducing agent or “developer.”

The silver halides employed are silver bromide, silver chloride and silver iodide. The first two may be used separately or combined, depending on the sensitivity and tonal qualities desired in the product. Silver iodide is always combined with silver bromide or silver chloride.

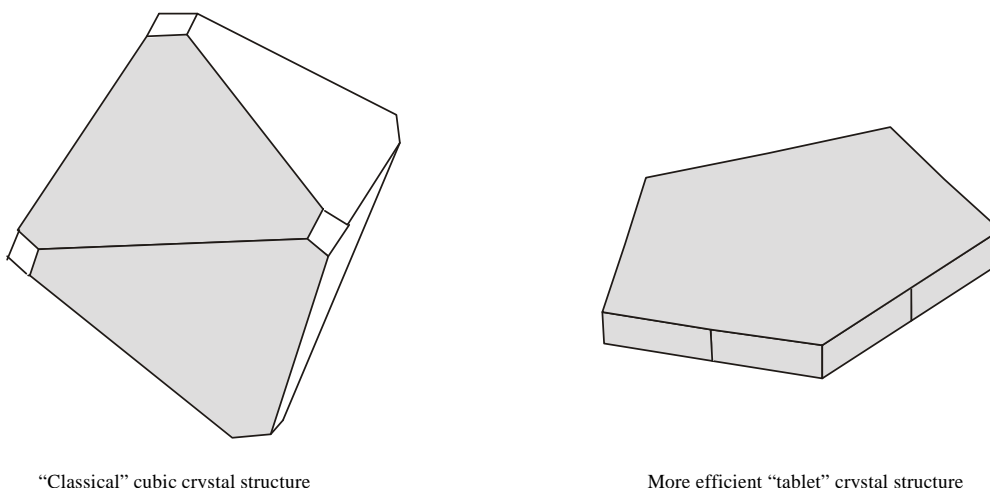


Figure 2: A schematic representation of cubic and “tablet” silver halide grains

As already noted, the silver halides used in photography are dispersions of microscopic crystals in a colloidal binder that is usually bone gelatin. Although such dispersions are referred to as emulsions or photographic emulsions, they are really dispersions.

When an exposed film is placed in a developer solution, the grains that contain silver nuclei are reduced much faster than those that do not. The more nuclei present in a given grain (i.e., the greater the exposure of that grain), the faster the reaction with developer and the darker the image at that site in the film. Factors such as temperature, concentration of the developer, pH, and the total number of nuclei in each grain determine the extent of development and the intensity of free silver (blackness) deposited in the film emulsion in a given time.

Not only must the developer be capable of reducing silver ions to free silver, but it must be selective enough not to reduce the unexposed grains, a process known as "fogging," within the time frame of the development process. Some substances that are commonly used as silver halide developers are listed in Table 1.



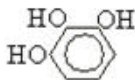

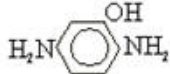
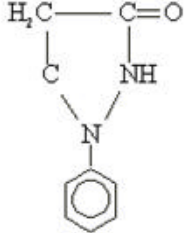
The developer is oxidized in the process. If not properly protected it can also be oxidized by air, a process that, if not prevented, will result in the loss of developer activity. To help

prevent such effects, commercial developer solutions commonly contain preservatives such as sodium sulfite.

Gelatin – The Film Matrix

Gelatin is a protein extracted from animal hides, bone, and sinew that belongs to the class of substances known as hydrophilic (“water loving”) polymers, which also includes other proteins, gums, starches, and a wide variety of synthetic polymers. Photographic grade gelatin is usually produced by an alkaline extraction process using bovine bones, although some acidic processes have been developed. Some special gelatins are also used that are derived from pigskins. The origin and quality of the raw materials used in the gelatin process, the conditions employed (pH, temperature, time, etc.), and the presence or absence of certain possible contaminants (e.g., mercury or other heavy metals, lipids, sulfur compounds, etc.) are of vital importance to the production of material suitable for use in modern photographic systems. In fact, photographic gelatin is much purer than that used in food applications.

Table 1: Common silver halide developers

Name	Structure
p-Dihydroxybenzene (Hydroquinone)	
Monomethylpaminophenol (Metol or Elon)	
1,2,3-Trihydroxybenzene (Pyrogallol)	
p-Aminophenol	
Diaminophenol (Amidol)	
1-Phenyl-3-pyrazolidone	

Gelatin solutions have the useful property of behaving as a liquid when warm and setting to a relatively hard gel when cool. When coated on a substrate and dried it is flexible and

reasonably resistant to physical damage, but it readily absorbs water (as in the development process). Generally, the coated gelatin dispersion will contain some material such as formaldehyde as a “hardener” that serves to produce a limited number of cross links among protein chains that improve the physical characteristics of the coated material. The gelatin swells rapidly, absorbing water and dissolved development chemicals, but it does not dissolve or disintegrate at normal temperatures. These properties are essential in the preparation of a photographic emulsion, in coating it on film base or paper, and in the processes of development, fixation and washing.

Gelatin is more than a means of holding the sensitive silver halide salts in place on a on a film base, however. It is an integral part of the process and can significantly affect the properties of the final photographic product. Controlling the characteristics of the gelatin is absolutely essential to the photographic emulsion preparation, the process of coating the emulsion on the film base, the adhesion of the coated material to the film base, the wetting characteristics of the coated material in the development process, the physical characteristics of the dried developed product, and the long-term stability of the developed image. In a way, one could safely say that the gelatin is almost as important as silver to the overall photographic system.

In the preparation of a photographic emulsion the gelatin also acts as an anti-coagulant or stabilizing colloid. The silver halide formed in fluid gelatin does not precipitate out of solution but remains uniformly distributed throughout the preparation, ripening (see below), and coating processes. The gelatin is an important factor in determining the dispersity or range of grain sizes of the silver halide. By suitable regulation of the concentration of the gel, the temperature, and the rate of addition of the components, the grain size distribution can be controlled to meet specific requirements.

In the silver halide dispersion, gelatin molecules adsorb at the surface of the silver halide grain, surrounding the grain and forming a barrier that stabilizes the dispersion. The adsorbed layer also, in all likelihood, affects the radiation sensitivity of the grain and makes reduction by developers, more controllable. This is important in the development process and makes it possible to obtain desired results from a given system based on easily controlled parameters such as developer chemistry, development time, temperature, etc.

Photographic Emulsion Preparation

The exact methods used in preparing commercial photographic emulsions are closely guarded trade secrets, but the basic procedures are well known. There are two general classes of emulsions, the characteristics of which are determined by the end use. They are “negative” emulsions that are used for exposure in cameras and produce a reversed or negative image, and print images that produce the final photograph that we show off to our friends and relatives.

Negative emulsions generally must exhibit a relatively wide flexibility in terms of sensitivity since they are used under conditions that are generally beyond the control of the casual photographer. It would be rather impractical if we couldn’t take our vacation pictures in bright sunlight and shade with the same camera and film. The professional photographer has the option of having several thousands of dollars of cameras dangling around her neck to suit the conditions. Most of us do not.

Print or paper materials, on the other hand, are used under highly controlled conditions of exposure and can therefore have a much more limited “range” of sensitivity and provide the

user with more direct control over the final results of the development process.

The preparation of a negative emulsion involves four distinct, but interrelated, steps: (1) the formation of silver halide crystals in gelatin through a precipitation process, (2) the recrystallization of the silver halide grains by physical or Ostwald ripening, (3) a washing process that removes excess soluble salts from the emulsion, and (4) a digestion or chemical sensitizing process involving the heating of the emulsion to increase its sensitivity to incident light.

The silver halide is formed through the reaction of a halide and ammoniacal silver nitrate, in a dilute (approximately 1.5 percent) solution of gelatin at a temperature between 45° and 70° C. The halide and the silver solutions may be added to the gelatin together, in what is termed a double-jet process, or separately (single-jet), in which case the halide is added first followed by the silver nitrate solution. The concentration of gelatin, the temperature, the concentrations of the two solutions and the rates of addition are important factors in determining both the average size and the size-distribution of the dispersion of silver halide and all must be carefully controlled.

After crystallization, the emulsion is stored for several hours at a moderate temperature during which the average crystal size increases via Ostwald ripening in which the smaller crystals tend to dissolve while the larger crystals grow as crystallization nuclei.

Following this ripening process the by-products are removed and the amount of free halide is reduced. Historically this was accomplished by chilling the emulsion to a gel and forcing it through a perforated screen to form "noodles" which were then washed in running water. Other methods, which are generally trade secrets, but include membrane filtration techniques, are now used in some cases.

After washing, additional gelatin is added to bring the emulsion to its final gelatin composition. Quite often, the added gelatin is rich in sulfur containing amino acids. The final emulsion is then heated to a temperature between 50° and 80°C for about an hour to facilitate the interaction of the sulfur in the added gelatin and the silver crystals. The sulfur-silver halide interaction increases the number and size of the silver sulfide sensitivity centers and improves the characteristics of the grains. An alkaline gold thiocyanate may also be added at this stage to increase the sensitivity of the emulsion.

Other additives to the final emulsion may include:

- (1) stabilizers to retard changes in the size and size distribution of the grains;
- (2) antifogging substances to retard the development of unexposed grains of silver halide when the image is developed;
- (3) a gelatin hardener to prevent the gelatin from excessive swelling in processing;
- (4) surfactants and other components to control the wetting and other fluid characteristics of the emulsion during the coating operation;
- (5) surfactants, lubricants, and anti-static agents to control the surface properties of the dried emulsion;
- (6) color-sensitizing dyes that expand the range of light sensitivity of the emulsion.

Because the printing of images on paper is carried out in the darkroom under closely controlled conditions, the light sensitivity of the emulsion is not as critical as other visual aspects of the final print such as the tone and contrast of the image.

The emulsions used for developing papers differ from negative emulsions in a number

of important respects. In preparing the paper photographic emulsion, the silver may be added to the gelatin solution containing the soluble halide, as in the preparation of a negative emulsion, the halide may be added to the gelatin silver solution, or the silver and soluble halide may be added simultaneously. The rate of addition and the concentrations involved are all designed to produce fine, uniformly sized crystals. In some processes, precipitation takes place in a slightly acid solution to inhibit recrystallization and growth of the crystal size. An excess of soluble halide is avoided for the same reason.

Paper emulsions are generally not heat ripened, as are negative systems, since that would result in larger average crystal sizes and tend to increase the sensitivity. Nor are they generally washed, because the concentration of salts is low and their presence tends to reduce further ripening in storage and changes in sensitivity. In addition, when the emulsion is coated on the paper, a significant amount of the soluble salts is absorbed by the paper stock and thus removed from the system. Those ions that remain in the emulsion may have a desirable influence on the color or contrast of the final image.

The speed or sensitivity of an emulsion can be adjusted in many cases by the use of color-sensitizing dyes (see below). Other additives may be antiseptics, such as phenol or thymol to inhibit the growth of microorganisms; hardeners, such as alum, formaldehyde and glyoxal to improve the physical characteristics of the emulsion during storage and development; and wetting agents, such as saponin or other surfactants to reduce surface tension and facilitate the coating of the emulsion.

Special papers with wider ranges of applicability in terms of contrast, spectral sensitivity, tonal qualities, etc., may be produced in one of two ways: (1) by the admixture of two emulsions of different contrast and color sensitivity, and (2) by sensitizing in such a way that the result varies with the wavelength of the exposing light.

The silver halide grains in a paper emulsion seldom exceed 0.01 to 0.02 microns as compared with from 1.0 to 2.0 microns in a negative emulsion and the amount of silver halide in the coated paper per unit area is about one-fifth that of a negative material.

Color Sensitizing

The radiation sensitivity of silver halides ends for all practical purposes at about 525 m μ . In Figure 3 Curve A illustrates the spectral sensitivity of a typical silver bromo-iodide emulsion and B illustrates the average human visual response curve. As the curves show, the maximum response of the eye is in the yellow-green near 550 m μ which lies beyond the sensitivity range of the emulsion, which is much more sensitive to the violet and blue than the eye.

The sensitivity of the silver halides may be extended to radiation of longer wavelengths by the addition of dyes or "color sensitizers." Although referred to as dyes, color sensitizers are not ordinary dyes in that they are not used to color cloth or other materials.

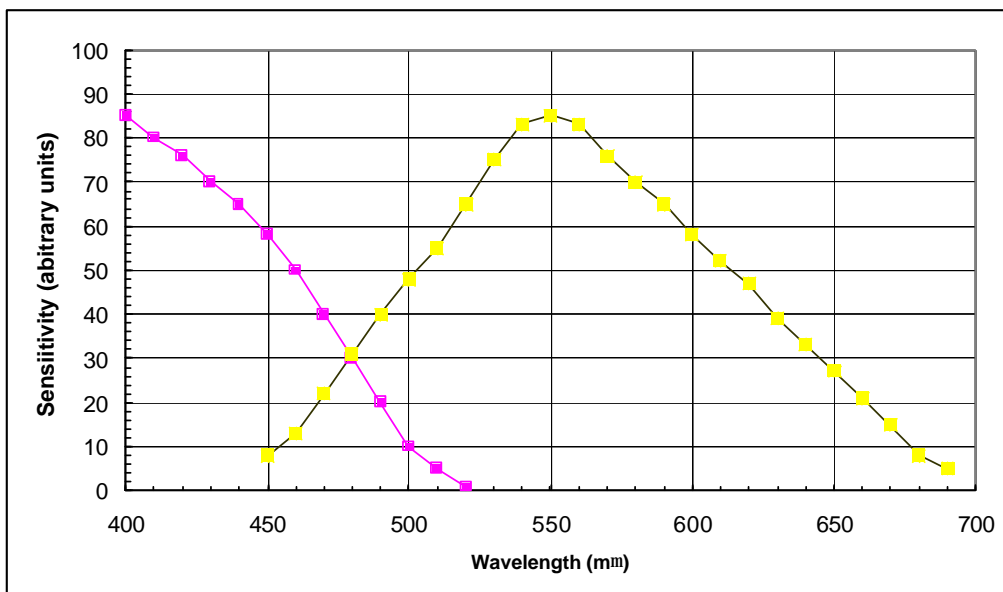


Figure 3: Curves approximating the light sensitivity of typical silver halide crystals (blue) and the human eye (yellow).

Emulsion sensitizing results from the absorption of radiant energy by the dye at a wavelength that would not affect the silver halide, and the transfer of that “exposure” energy to the silver halide to form a latent image and make the affected grain developable. If a dye is a sensitizer, then its action depends upon the absorption characteristics of the silver halide-adsorbed color sensitizer complex, which may be quite different from the absorption of the dye itself. Since the sensitivity of such dyes varies greatly, it is often necessary to use a combination of materials to obtain a specific result. Some combinations, however, do not work well together, so that the system balance must be carefully studied before the final emulsion composition is determined. There are substances that may or may not be sensitizers themselves but greatly increase the sensitizing action of other dyes. These are known as super-sensitizers and are of considerable importance in facilitating the use of conventional sensitizing dyes. Whatever the dye used, the quantity required is always quite small.

Development

The rate of development of the individual grains in an emulsion is affected by so many factors, such as the rate of diffusion of the solution through the gelatin matrix, the adsorption of the developing agent, the solution of the silver halide, oxidation products of the developing agent and the accumulation of restraining by-products, that exact analysis of it is difficult. The time of appearance of a visible image is, within limits, a reliable indication of the rate of development. It varies with different emulsions and is quite different with different developing agents, but the variation with temperature, dilution and pH is almost directly related to the variation in the rate of development.

The rate of development, as determined from the change in the optical density of the developed image, is complicated by the fact that density increases in two different ways: (1) by

the increase in the amount of silver as the grains develop and (2) by an increase in the number of grains in the process of development. Density grows rapidly at first and then slows down until development is complete and no further growth in density takes place. Prolonged development would, of course, increase overall density through the development of unexposed grains (fog).

Halting Development – the Stop Bath

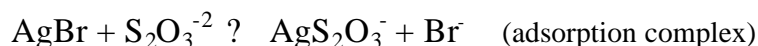
Once the exposed image has been developed to the desired degree, it is necessary to halt the chemical process quickly to prevent over development and the production of fog. The solution used to that end is referred to as the “stop” bath. Since developers function a relatively high pH’s, the typical stop bath is simply a solution of acetic or some other weak acid. The action of the acid is so rapid it usually requires only seconds for the process to be effectively halted.

The Fixing Process

Once the developed image is obtained, a large amount of unexposed and undeveloped silver halide remains in the emulsion. If that silver halide is not removed before the image is exposed to radiation capable of producing a latent image, the image will continue to darken. The process of removing the residual silver halide from the image is called “fixing.”

The silver halides are only slightly soluble in water; therefore, to remove the material remaining after development it is necessary to convert it to soluble complexes which can be removed by washing. Sodium thiosulfate, commonly termed “hypo,” has been used for this purpose since 1839.

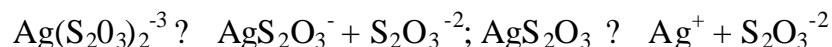
The reactions in fixing can be written as follows:



which is followed by



and by



Within limits, the rate of fixation is indicated by the clearing time, i.e., the time required to remove all visible traces of silver halide from the image. This time depends on the concentration of thiosulfate, the temperature, the agitation of the solution, but more particularly on the emulsion and the extent to which the fixing bath has been used. Fine-grain emulsions fix in less time than those of larger grains, and paper emulsions of silver chloride fix faster than bromo-iodide negative emulsions. Thickly coated films, other things being equal, fix more slowly than those with a thin emulsion coating. The fixing time increases appreciably as the solution becomes depleted. With continued use the halide-ion concentration rises in proportion

to the amount of silver halide dissolved. When the product of the silver-ion and the halide-ion activities reaches the solubility product of the least soluble silver halide present, the solution will dissolve no more of that silver halide and fixation will necessarily be incomplete

It is usually desirable to harden the gelatin after development, and while this may be accomplished by a hardening stop bath prior to fixing, the usual practice is to combine hardening with fixing. The conventional fixing and hardening bath contains in addition to the fixing agent:

1. An organic acid, usually acetic, to provide the necessary acidity to stop development and create the proper pH for effective hardening.
2. Sodium sulfite, which prevents the decomposition of the thiosulfate by the acid and forms colorless oxidation products of the developer thus preventing staining.
3. Alum as a hardening agent.

The hardening produced by alum is due to the reaction of the aluminum ions, Al^{+3} , and the carboxyl groups of the gelatin with the formation of cross-linkages between chain molecules. The degree of hardening, other things such as temperature, alkalinity of the film when placed in the fixing bath, etc., being equal, depends on the pH of the solution which in turn depends on the relative proportions of acid, sulfite and alum.

Since the addition of developer tends to increase the pH of the fixing bath, the solution should be buffered against an increase in pH. For this reason weak organic acids, such as acetic acid, are used in preference to a stronger acid, such as sulfuric. The addition of boric acid increases the useful hardening life of potassium alum baths and reduces the tendency of the bath to form a sludge.

References and Further Reading

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