Silver Halide Materials

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Silver Halide is the most common holographic material currently used by everyone from hobbyists to professional scientists. This is because of its high sensitivity and the fact that it's easily available commercially. Silver Halide is a salt of Silver and a Halide, which are a group of elements that include Fluorine, Chlorine, Bromine and Iodine, which are light sensitive. The first, accidental, discovery of the light sensitive properties of Silver salts came in 1727 when J Schulze mixed chalk, Nitric acid and Silver in a flask. He noticed that the side of the flask turned toward the sun turned dark. The first deliberate application of this effect, a photograph of a scene, was carried out by Niepce in 1827. This was a long exposure of about 8 hours. In 1841 Henry Fox Talbot patented a "calotype" process which made a permanent negative image on paper soaked in Silver Chloride. The present day emulsion was created by Richard Leach Maddox, who proposed using gelatin and Silver Bromide in what he called the "dry plate process". Shortly after that Eastman Kodak coated a flexible film with this as a thin emulsion, mass produced it, and launched large scale photography. Silver Bromide is only sensitive in the UV and blue regions and so dyes need to be added to it in order to make it sensitive to other colors. In holography, specific dyes are added to give the emulsion a high sensitivity at particular, commonly available laser lines.

Commercial SilverHalide materials consist of crystals, or *grains*, of Silver Halide dispersed in a layer of gelatin, each grain consisting of many thousands of molecules of Silver Halide. When exposed to light individual molecules of Silver Halide on those grains that were illuminated break down to Silver which, due to it's small size, appears black. Since the number of molecules of Silver Halide that convert to Silver on any one grain depends on the intensity of light hitting the grain, the darkness, or density, of any one grain depends on the light hitting it. Thus the emulsion converts the variation of light that hits it, the *exposure,* to a density variation. After exposure the emulsion consists of exposed and unexposed Silver Halide grains. The action of converting the exposed emulsion to the same variation of density as the variation of light intensity at exposure by amplifying the exposed grains of Silver Halide is known as *processing*. The removal of the unexposed grains is known as *fixing*. Thus the entire process consists of exposure, development and fixing. There is also a bleaching step that is no longer widely used in photography but is common in holography. The fixing step is sometimes omitted.

Exposure

The exposure of an emulsion refers to the total amount of light energy that has hit it over a given period of time, the *exposure time*. In holography, this is referred to as the *sensitivity* or *speed* of the emulsion and is given in terms of Joules/sq meter. However, due to the extremely high sensitivity of Silver Halide emulsions, this is usually given as microjoules/sq cm. This is the amount of energy necessary in order to produce a certain variation of darkness in the emulsion that faithfully maps the light that hit it. Too much exposure and the entire film goes black, too little and there is little or no variation of darkness. Factors important for exposure are the *resolving power* of the film and the contrast.. The resolving power of a film determines the smallest detail that the film can captured. In holography, these details are in the order of a micron and so holographic film needs to have a very high resolving power. This resolving power depends on the size and distribution of the individual grains in the emulsion, referred to as the *granularity*. In photographic film, the size of the grains may be about a micron whereas in holography it's usually about 50 nanometers. As the grains get smaller, the sensitivity decreases, i.e. it takes a longer exposure time to create the same density variation. Another factor that affects resolving power is the *scatterin*g within the emulsion. This refers to the fact that the light entering the emulsion is scattered into random directions by the grains themselves. This randomly scattered light will affect nearby grains and so will decrease the resolving power. A measure of this resolving power is given by a curve plotting density against the logarithm of the exposure, known as the Hurter and Driffield, or H&D curve. The slope of this curve is known as the *gamma.* Typical values of gamma for standard photography are about 0.7 while high contrast film has a gamma of about 1.5. In holography, it is necessary to have a gamma of at least 2. After exposure, the emulsion contains an invisible image called the *latent image* in which some of the grains in the emulsion were exposed to light and some were not. These exposed, latent image grains are distinguished from non-exposed grains by the their ability to be reduced to elemental Silver by the developer.

Development

All the grains in the emulsion consist largely of Silver Bromide with a few atoms of free, elemental Silver, called *sensitivity specks*. These Silver specks contain about 1/10,000,000 of the mass of the whole grain. When a particular grain is exposed to light, some of the Silver specks on it are ionised by the release an electron. These Silver ions cause neighbouring Silver from nearby Silver Bromide molecules on the grain to also reduce to elemental Silver and hence the speck grows to form a larger latent image-speck. When the speck has grown to a particular size, it provides a point at which the developer can attack the grain. Grains which have not been exposed to light will still have specks, but with no ionisation of the specks, they will not grow sufficiently to form development centres.

Developers consist of the following components:

Developing agent
Preservative
Accelerator
Restrainer or anti-foggant

Developing agent

The developing agent is responsible for the reduction of all the Silver Bromide in the entire exposed grain into Silver, these grains being differentiated from the unexposed ones due to the presence of latent image specks. This results in an enormous amplification of the latent image by a factor of about 10,000,000. This is due to the fact that the mass of Silver in the original, undeveloped latent image speck was only about 1/10,000,000 th of the mass of the grain. Development causes the entire grain to convert to Silver. The developing agent is an organic reducing agent with a benzene ring-type structure.

Preservative

Developing agents tend to oxidize rapidly when exposed to air making them ineffictive. To prevent this, a preservative is added. Usually this is Sodium Sulphite but sometimes Potassium Sulphite is used. As the sulphite concentration is increased, the developer lasts a longer time. However, if too much sulphite is added, the emulsion may fog.

Accelerator

Developing agents only work when they are alkaline, with increasing activity as the alkalinity increases. An accelerator is an alkaline compound that activates and accelerates the developing action. The accelerators are classed as strong, medium and weak. The stronger the accelerator, the more rapid the development while weak accelerators tend to balance out contrast. Strong accelerators include hydroxides, such as Potassium Hydroxide, medium accelerators include Carbonates, such as Sodium Carbonate.

Restrainer or Antifoggant

Some developers tend to attack unexposed grains which causes fog in the emulsion. To prevent this an antifoggant, or restariner, is added. The most common restrainer is Sodium Bromide. Some low alkalinity developers may not need restrainers.

Fixing

After development the emulsion consists of grains of Silver, formed by the reduction of exposed Silver Halide, and unexposed Silver Halide grains. Fixing removes these unexposed Silver Halide grains rendering the emulsion inert to further reactions from light. The fixer is a solution of Sodium Thiosulphate which converts the Silver Bromide into Silver Thiosulphate and a few other ions. Ammonium is used in place of Silver in Rapid Fix due to the stronger solvent action. Of Ammonium Thiosulphate. The Silver Thiosulphate is very soluble in water and washes out of the emulsion and into the fixing bath. However, if the concentration of the Silver ions in the fixing bath is too high other, less soluble, Silver salts are formed. These can cause a yellowing of the emulsion.

Commercial fixers also include a weak acid, usually acetic acid, to stop the action of the developer. The pH of the fixer is then about 4 or 5. If the pH decreases to too low a value (ie it becomes too acidic), the acid attacks the Thiosulphate and releases free Sulphur, This free sulphur forms a suspension in the emulsion causing it to fog.

A hardener is sometimes also added to prevent swelling and softening of the gelatin during the wash. This is accomplished by lowering the pH of the fixer by a suitable agent to a value of about 3.

Bleaching

Bleaching is the action of an oxidising agent on the Silver grains. The oxidising agent oxidises the Silver to a soluble salt, that can be washed. The purpose of bleaching a hologram is transform the reconstruction method of the hologram from one whose primary reconstruction method is by altering the intensity of the reconstruction light - known as an *amplitude hologram* - to one whose primary reconstruction method is by altering the phase of the reconstructing light - known as a *phase hologram*. In the former, amplitude-type hologram, the intensity of the (uniform) reconstructing beam is decreased as it passes through various parts of the hologram by an amount depending on how dark that particular part of the hologram is. The image is therefore dependant on the variations of the intensity of the reconstruction beam which is a map of the darkness variation of the plate. In the phase-type hologram, the hologram is completely transparent but either it's thickness or it's density varies at different points of the holographic medium thus altering the rerfractive index at that perticular point. This variation of index alters the optical light path of the reconstruction beam as it passes through different parts of the holographic medium. In practice no hologram is ever completely of one or the other type, but a mixture of the two. This variation of index in a medium is known as *phase variation*. It has been shown that the brightness, or *diffraction efficiency*, of an amplitude hologram cannot exceed 33% while a phase hologram can be 100% efficient. However when a Silver Halide hologram is developed it is, by default, an amplitude hologram, due to the fact that the developer's action varies the density of the medium. It would therefore be advantageous to convert the amplitude hologram to a phase hologram. This is done by a bleach which makes the entire holographic medium transparent and transforms the density variations of the medium into index variations.

There are essentially two types of bleaches - reversal and rehalogenating. In reversal bleaches, the exposed, Silver grains are converted into a soluble complex and washed out in the bleach bath leaving the unexposed Silver Halide grains left in the emulsion to carry the holographic image. In this case, it's necessary not to fix the hologram after developing since the loss of the unexposed Silver Halide would leave nothing in the emulsion. A reversal bleach bath consists of an oxidising agent , a buffer and sometimes other additives such as dyes.

In rehalogenating bleaches, the reduced Silver grains are re-converted back to Silver Halide. Rehalogenated bleaching can be carried out on either fixed or unfixed holograms. In the fixed rehalogenating case, the unexposed Silver Halide is fixed out and the rehalogenating bleach converts the exposed Silver back to Silver Halide. In unfixed rehalogenation, the unexposed Silver Halide grains are still present after the bleach converts exposed Silver grains to Silver Halide grains. The difference between the two, necessary to distinguish image from non-image, comes from the fact that rehalogenated Silver Halide grains are larger than the original unexposed Silver Halide grains. One consequence of the increased size of the grain is that there is an increase in noise since scattering is dependant on, and increases with, larger grain sizes. A rehalogenating bleach bath consists of an oxidising agent, an alkali halide, a buffer and sometimes dyes.

<u>*References*</u>

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