

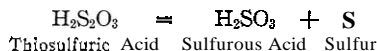
CHEMISTRY FOR THE AMATEUR PHOTOGRAPHER. IV. FIXATION AND WASHING*

The Chemistry of Fixation

After development, the undeveloped silver bromide is removed by immersion of the negative or print in what is called the "fixing" bath. There are only a few substances which will dissolve silver bromide, and the one which is universally used in modern photography is sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, which is known to photographers as hyposulfite of soda, or more usually as hypo, though the name hyposulfite of soda is used by chemists for another substance ($\text{Na}_2\text{S}_2\text{O}_4$).

Fixing is accomplished by means of hypo only, but materials are usually transferred from the developer to the fixing bath with very little rinsing so that a good deal of developer is carried over into the fixing bath, and this soon oxidizes in the bath, turning it brown, and staining negatives or prints. In order to avoid this the bath has sodium sulfite added to it as a preservative against oxidation, and the preservative action is, of course, greater if the bath is kept in a slightly acid state. In order to prevent the gelatin from swelling and softening it is also usual to add some hardening agent to the fixing bath so that a fixing bath, instead of containing only hypo, will contain in addition sulfite, acid, and hardener.

If a few drops of acid, such as sulfuric or hydrochloric, are added to a weak solution of hypo, the hypo will be decomposed and the solution will become milky, owing to the precipitation of sulfur. This is because the acid converts the sodium thiosulfate into the free thiosulfuric acid, and this substance is quite unstable, decomposing into sulfurous acid and sulfur according to the equation:



The change of thiosulfate into sulfite and sulfur is reversible, since, if we boil together sulfite and sulfur we shall get thiosulfate formed, so that while acids liberate sulfur from the hypo, sulfite combines with the sulfur to form hypo again. Consequently, we can prevent acid decomposing the hypo if we have enough sulfite present, since the sulfite works in the opposite direction to the acid. An acid fixing bath, therefore, is preserved from decomposition by the sulfite, which also serves to prevent the oxidation of developer carried over into it. The developer which is carried over into the fixing bath is, however, alkaline and consequently a considerable quantity of acid is required in a fixing bath which is used for any length of time, since if only a small quantity is present, it will soon be neutralized by the developer carried over. We are, therefore, in the

* This series of articles is based upon selected chapters from "Elementary Photographic Chemistry" and "The Fundamentals of Photography." by Dr. C. E. K. Mees, published by the Eastman Kodak Company, Rochester, New York.

difficult position that we require a large quantity of acid present, and yet the fixing bath must not be strongly acid. The solution of the difficulty is found by taking advantage of the fact that there are some acids which are very weak in their acidity and yet **can** neutralize alkali in the same way as a strong acid, so that a large quantity of these acids can be added without making the bath so acid that sulfur is precipitated.

The strength of an acid depends upon the fact that when it is dissolved in water some of the hydrogen contained in it dissociates from the acid and remains in the solution in an active (or ionic) form, **and** the acidity of the solution depends upon the proportion of the hydrogen which is dissociated into the ionic form. The quantity of alkali which the acid can neutralize, however, depends upon the total quantity of the hydrogen present, and not on the dissociated portions only. The strongest acids are the mineral acids, such as sulfuric and hydrochloric, while the weakest acids are the organic acids, such as citric and acetic.

Since a large quantity of a weak acid is required, the best acid for the purpose is acetic acid (CH_3COOH).

When acetic acid cannot be obtained for the fixing bath, the only substitute which appears to be generally available is sodium bisulfite, NaHSO_3 . This compound is intermediate between sodium sulfite and sulfurous acid, and is, therefore, equal in acidity to a mixture of equal proportions of these two substances. It makes a satisfactory acid fixing bath but does not give quite as good a reserve of available acid in the bath as acetic acid does. This is of importance particularly in connection with the hardening agent used in the fixing bath.

Potassium alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, is the commonest hardening agent. The alums in general have the property of tanning gelatin.

Fixing Baths

Acid hardening fixing baths are prepared by adding to hypo an acid hardening solution which contains the following ingredients:

- (a) An acid such as acetic, citric, tartaric, lactic, malic, **maleic**, sulfuric, etc., which stops development.
- (b) A hardening agent **such** as potassium alum, potassium chrome alum, or formaldehyde, 40%.
- (c) A preservative such as sodium sulfite or sodium bisulfite. The latter acts as preservative in two ways: it prevents the formation of sulfur by the action of the acid on the hypo, while it also prevents the developer carried over into the fixing bath from oxidizing and turning brown.

Prepare the acid hardening solution as a separate stock solution and add this to the hypo solution as required.

The order of mixing is important, as follows:

When mixing in one vessel, first dissolve the sulfite in warm water (about 125°F.) (52°C.), then add the acid and then the potassium alum. It is sometimes recommended to reverse the process, namely, dissolve the alum first, add the acid, and then the sulfite, but the alum dissolves more readily in the acid-sulfite solution.

Another method is to dissolve the alum and sulfite in separate solutions, cool, add the acid to the sulfite solution and then add the alum solution.

The hypo should be cool and dissolved completely before adding the cool hardener; otherwise sulfur is likely to be precipitated.

If the order of mixing is reversed and the alum added first to the sulfite, a white sludge of aluminum sulfite is formed which dissolves with difficulty when the acid is added. Therefore, if after mixing the hardener is milky and a sludge settles out, it is due to a relative insufficiency of acid; that is, the acid used was either not up to strength or too much alum or sulfite was added.

With other hardening baths the order of mixing is usually the same.

Acid Hardening Firing Bath for Films, Plates, and Papers

	Avoirdupois	Metric
Hypo	16 ounces	480.0 grams
Water to make	64 ounces	2.0 liters

Then add the following hardener solution slowly to the cool hypo solution while stirring the latter rapidly.

Water (about 125°F.) (52°C.)	5 ounces	160.0 cc.
Sodium sulfite	1 ounce	30.0 grams
Acetic acid (28% pure) ¹	3 ounces	96.0 cc.
Powdered potassium alum	1 ounce	30.0 grams

Dissolve in the order given.

If it is desired to mix a stock hardener solution, use:

Acid Hardener Stock Solution

	Avoirdupois	Metric
Water (about 125°F.) (52°C.)	56 ounces	1700.0 cc.
Sodium sulfite	16 ounces	480.0 grams
Acetic acid (28% pure) ¹	48 ounces	1500.0 cc.
Powdered potassium alum	16 ounces	480.0 grams
Cold water to make	1 gallon	4.0 liters

For use, add 1 part of cool stock solution slowly with stirring, to 8 parts of a 25% cool hypo solution.

To make up the hardener dissolve the chemicals in the order given above. The sodium sulfite should be dissolved completely before adding the

¹ To make 28% acetic acid from glacial acetic add, dilute three parts of glacial acid with eight parts of water.

acetic acid. After the sulfite-acid solution has been mixed thoroughly, add the potassium alum with constant stirring. If the hypo is not thoroughly dissolved before adding the hardener a precipitate of sulfur is likely to form.

The Useful **Life** of Fixing Baths

A fixing bath in use becomes exhausted as a result of performing useful work in fixing out the emulsion. The acidity of the bath is being reduced by the developer carried in, although at first this tends to favor a longer "sulfurization life" or period of time before the bath precipitates sulfur. With use, however, the solution finally reaches a point where a sludge of aluminum sulfite is precipitated, rendering the bath useless. During the first stages of use, the hardening properties increase slightly, after which they fall off rapidly. A fixing bath is usually exhausted if it froths at the surface, or if it becomes milky or sludges throughout the solution. The bath may also fix so slowly that there is danger of removing the films or prints before they are completely fixed. When the time of clearing for a slow fixing film exceeds 12 to 16 minutes, the bath should be discarded.

The fixing bath for which directions have been given will fix completely the equivalent of one hundred 8" X 10" prints per gallon, provided a thorough water rinse precedes fixation.

Recovery of Silver from Exhausted Fixing Baths

An exhausted fixing bath contains dissolved silver salts and various methods may be employed to recover the silver profitably, providing at least 6 gallons of well-exhausted hypo are discarded each week. For large volumes of exhausted baths (about 100 gallons or more per week) precipitation with sodium sulfide is the most economical and rapid method. Precipitation with zinc dust is efficient when smaller volumes of bath are to be treated, and has the advantage that no objectionable fumes of hydrogen sulfide are evolved, as in the sulfide process.

Recovery by means of commercial electrolytic units also represents a simple and economical procedure for volumes of exhausted baths of less than 100 gallons per week. Electrolytic units give best results when used in a discarded fixing bath, rather than in a working bath.

Although it is possible for a capable chemist to so restore a fixing bath by desilvering, subsequently clarifying, and modifying its composition, that its useful life is prolonged, it is just as economical and preferable to prepare a fresh bath.

Fixing Bath Troubles

A. Sludging of the Fixing Bath: A fixing bath occasionally turns milky soon after the hardener is added, and sometimes after being in use for a short time. The milkiness may be of two kinds:

1. If the precipitate is *pale* yellow and settles very slowly on standing, it consists of sulfur and may be caused by (a) too much acid in the hardener; (b) too little sulfite or the use of impure sulfite, in which case there is not sufficient present to protect the hypo from the acid; (c) high temperature. The hardener should only be added to the hypo solution when at room temperature. If the temperature of the acid fixing bath is over 85°F. (29°C.), it will not remain clear longer than a few days even when mixed correctly. The only remedy is to throw the bath away and mix fresh solution as required.

If a **sulfurized** bath is used, the sulfur is apt to penetrate the gelatin, and later may cause fading of the image.

2. If the precipitate is white, and a gelatinous sludge of aluminum sulfite settles on standing, it may be caused by (*a*) too little acids in the hardener; for example, supposing a formula calls for pure glacial acetic acid and 28% acid is used by mistake, then less than **one-third** the required concentration of acid is present; (*b*) too little hardener in the fixing bath. When fixing prints, a relatively large proportion of the developer is carried over to the fixing bath (unless a water or acid rinse bath has been used) which soon neutralizes the acid, and therefore increases the tendency for precipitation of aluminum sulfite. In the same way a fixing bath with the correct proportion of hardener, when exhausted, still contains alum and sulfite but no acid, and these combine to form a sludge of aluminum sulfite.

B. The bath does not harden *satisfactorily*. Insufficient hardening may be a result of (1) the use of inferior alum which does not contain the correct proportion of aluminum sulfate; (2) the presence of too much acid or sulfite; or (3) an insufficient quantity of alum. On varying the proportions of acid, alum, and sulfite in a fixing bath, it has been found that the hardening increases as the quantity of alum increases. With increasing quantities of acetic acid, with a given quantity of alum, the hardening increases to a maximum, beyond which it decreases until the solution does not harden at all. A certain minimum quantity of acetic acid, however, is necessary to give the fixing bath a fairly long, useful life, before aluminum sulfite precipitates, but this quantity is usually greater than the quantity which produces maximum hardening. With **use**, therefore, the hardening ability of most fixing baths at first increases with the addition of developer to a maximum, beyond which the hardening falls off rapidly.

C. Blisters. When the sodium carbonate of the developer is neutralized by the acid in the fixing bath, carbon dioxide gas is evolved which **produces** blisters if the gelatin is too soft to withstand the disruptive action of the gas. If the fixing bath contains an excess of acid and the films are not rinsed sufficiently, or if a strongly acid rinse bath is used, blisters are apt to be formed. On dry film, blisters appear as tiny crater-like

depressions when examined by reflected light. This trouble is more liable to occur in hot weather, and especially when the bath is not hardening sufficiently.

D. Dichroic Fog. If the fixing bath does not contain acid or if it is old and exhausted and contains an excess of dissolved silver salts, a stain called *dichroic fog* is sometimes produced on the **film**. In reflected light, **film** stained in this way appears yellowish green and by transmitted light it looks **reddish-pink**. Dichroic fog never occurs in a fresh acid fixing bath, or if the film is rinsed before **fixing** and the temperature of the bath is kept at 65 to 70°F. (18 to 21°C.).

E. Scum on Fixing Baths. When a partially exhausted fixing bath is allowed to stand several days without use, the hydrogen sulfide gas usually present in the air reacts with the silver thiosulfate in the **bath** and forms a metallic appearing scum on the surface of the solution. This scum consists of silver sulfide and should be removed by drawing the edge of a sheet of blotting paper across the surface of the bath, or by using a skimmer made of several strips of cheese-cloth stretched over a wire frame.

A white scum consisting of aluminum **sulfite** is found sometimes on **films** or prints. This is caused by: (1) insufficient rinsing after development; (2) too low a concentration of acid in the fixing bath; (3) insufficient agitation of the **film** on first immersing in the fixing bath. Since aluminum sulfite is soluble in alkali, the scum may be removed by swabbing the film or print with a 10% solution of sodium carbonate and then washing thoroughly.

F. Mottle. When processing film or plates in **hangers**, a mottled image is occasionally found when the hanger has not been agitated enough on first immersing in the fixing bath, or if the film is insufficiently rinsed between development and fixation. In the absence of thorough rinsing and agitation, development continues **locally** during the first few minutes of fixing and in these spots the image has greater density. Mottle is also produced if the ends of the hanger protrude above the surface of the fixing bath, especially during the first stages of fixation.

The Chemistry of Washing

Washing is not usually regarded as a chemical operation. Nevertheless, the laws governing washing are distinctly chemical in their nature, and the importance of **washing** in photography justifies greater attention than is usually paid to the subject.

As a general rule the object in washing negatives or prints is to remove from them the chemicals of the fixing bath which they contain. In the first place, it must be pointed out that it should not be necessary to wash out silver compounds but only the chemicals of the fixing bath. If an exhausted fixing bath is used silver compounds will be present during

washing and must be removed very completely, so that if work has to be hurried and the time of washing must be cut down, it is most important that fixing should be complete.

The best way of insuring complete fixing is to use two fixing baths, and to transfer the negatives or prints to the second bath after they have been fixed in the first. Then, when the first bath begins to show signs of exhaustion and refuses to fix quickly, it should be replaced by the second, and the new, clean fixing bath should be used in the place of the second bath again.

The rate of washing depends largely upon the rate of diffusion of the hypo out of the film into the water, providing the water in contact with the film is continuously removed. This diffusion rate has nothing to do with solubility. The solubility of a substance fixes the proportion of the substance which can go into solution.

There are a number of errors which are current concerning washing. It is commonly believed, for instance, that plates and paper can be washed more rapidly in warm water than in cold. This is a mistake. It is true that any salt will diffuse more rapidly in warm water than in cold, but when washing a photographic material the diffusion has to take place in gelatin and the warmer the water in which the gelatin is placed, the more it swells, and its swelling hinders diffusion in about the same proportion as the rise in temperature accelerates it, so that, as a matter of fact, washing goes on at about the same rate at all ordinary temperatures.

It is sometimes stated that material which has been hardened in the fixing bath washes more slowly than material which has not been hardened. This, too, is incorrect. Gelatin is like a sponge; the effect of hardening it is to contract all the network of the sponge, but in so doing the gelatin as a whole is not contracted and there is no difference in the diffusion between gelatin, which has not been hardened and which has been hardened, unless the gelatin has been dried after hardening. If a negative is thoroughly hardened in the fixing bath and then is dried down, it will not expand much when soaked again and consequently diffusion through it will be difficult, but before drying the hardening does not affect diffusion and the materials which wash most quickly are those in which the gelatin has not been swollen in its treatment, either in development or fixation, but has been kept in a firm, solid condition.

The actual rate of washing may be understood by remembering that the quantity of hypo remaining in the gelatin is continually halved in the same period of time as the washing proceeds. An average negative, for instance, will give up half its hypo in fifteen seconds when washed directly under the faucet, so that at the end of fifteen seconds half the hypo will be remaining in it, after thirty seconds one-quarter, after forty-five seconds one-eighth, after one minute one-sixteenth, and so on. It will be seen that in

a short time the quantity of hypo remaining will be infinitesimal. This, however, assumes that the negative is continually exposed to fresh water, which is the most important matter in arranging the washing of either negatives or prints.

In most trays and washing tanks an average negative will give up half its hypo in 30 seconds. The process will then stop unless the water in the vessel is changed. The rate of washing thus turns out to be dependent firstly, on the degree of agitation, and secondly, on the rate of removal of the used water. This rate is dependent directly on the ratio of the stream of water falling into the vessel and the size of the vessel, quickest renewal taking place when the vessel is small and the stream large.

Only exact experimental measurements will tell when a particular vessel and stream of water will wash a specific kind of film or paper.

However, as a rough and safe working guide, the washing power of the vessel may be judged by noting the time it takes colored water to be replaced by colorless water from the faucet. To this time the minimum washing time for the material is added, and the total taken to indicate the actual period to be allowed by the photographer under his particular conditions.

A practical example will make the matter clear. Suppose that a large tray is resting in the sink and water is **falling** into it from the faucet and flowing to waste over the sides. Into the tray, and while the water is running, an ounce of 1% potassium **permanganate** solution or red ink is poured in and the time noted for the water to **become** completely colorless. To this time is added the minimum **washing** time of the material, a representative list of which is given below:

Lantern slide plates	3 minutes
Other plates	5 minutes
Film negatives, all kinds	about 7 minutes
Single weight Velox	15 to 20 minutes
Single weight Bromide	20 to 25 minutes
Double weight Bromide	35 to 60 minutes

If it be found that the water in the tray takes 10 minutes to clear, then the time for a lantern plate to become thoroughly washed would be 13 minutes and for Velox about 25 minutes. If the water supply were doubled and the rate of color discharge shortened to 5 minutes the washing times would be 8 minutes and 20 minutes, respectively. Finally, if the lantern plate were held under an open faucet in the hand, the renewal of water at the emulsion surface would be extremely rapid and the plate would be safely **washed** in **3 minutes**. The moral is to use plenty of water and plenty of agitation.

If a lot of prints are put in a tray and water allowed to splash on the top of the prints, it is very easy for the water on the top to run off again, and

for the prints at the bottom to lie soaking in a pool of fairly strong hypo solution, which is much heavier than water and which will fall to the bottom of the tray. If the quickest washing is desired, washing tanks should be arranged so that the water is changed continuously and completely and the prints or negatives are subjected to a continuous current of fresh water. If water is of value, and it is desired to economize in its use, then by far the most effective way of washing is to use successive changes of small volumes of water, putting the prints first in one tray for two to five minutes, and then transferring them to an entirely fresh lot of water, and repeating this procedure about six times.

Now a word of warning about contaminating partly washed photographs. If the hypo comes out to half its previous strength in a fraction of a minute, so also will the reverse change occur. If a partly washed print is touched by fingers contaminated with the fixing bath, in a few seconds the hypo will be shared between the fingers and the photograph, and it will take the full washing time to remove it again.

Since hypo is invisible and its evil effects are not detected till long afterward, prints or films fresh from the hypo should never be placed among those partly washed. If this is done the entire batch must be washed from the time that the last one was added.

The best way to avoid **contamination** is to wash in **cascade**. In its simplest form this can be accomplished by placing two trays side by side, one an inch or so above the level of the other. Water is allowed to run into the upper tray and overflow into the lower. **All** prints and films should be placed in the lower tray before transference to the upper. The operator should also use the lower tray for washing hypo off his fingers. The prints and films should have at least three minutes preliminary washing before going into the true **washing** tray. With a little experience in handling materials in this serial order the photographer will be surprised at the number of films and papers that can be passed through quite moderate capacity **trays** and completely satisfactory washing secured in a short time.

The progress of washing can be followed by removing two or three prints at intervals from the bath and testing for hypo by tasting the prints since hypo containing silver has a sweet taste.

Six changes of water, allowing five minutes for each change, should be sufficient to eliminate the hypo effectively from any ordinary photographic material.

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