Stop Baths and Fixers

Surely, it is the result that counts, no matter how it is achieved. A photographer can even become a prisoner of his own rules. Unless he invents new ones, he will soon copy himself, and his work will become sterile and repetitive.

—Bill Brandt

STOP BATHS

It is important to provide a buffer between the developer and the fixer. This is because the fixer will rapidly exhaust if it is contaminated with developer. Maintaining the activity of the fixer is of utmost importance to the longevity of negatives and prints.

Whether or not to use an acid stop bath or a plain running-water bath has been a long-standing controversy among photographers. There are two reasons cited for using an acid stop bath. First, it arrests development in the shortest possible time. The second is, "That's the way I was taught."

Even so, the disadvantages to using acid stop bath are:

- When sodium carbonate, one of the most commonly used alkali in film developers, comes into contact with acid, carbon dioxide gas is released which can cause blistering in the emulsion of both film and paper. The problem is more critical in film where it is appears as a pinhole, usually in dense areas of silver deposits such as the sky.

  If an acid bath is to be used there are two methods to prevent pinholes from occurring.

  1. Use developers compounded with mild alkali, either sodium metaborate or borax, which do not create carbon dioxide gas.
  2. Use a 3% to 5% solution of sodium metabisulfite, a 3% solution of chrome alum, or a mildly acid stop bath, such as Kodak SB-1 Nonhardening Stop Bath. Or use a very gentle-acting stop bath, suggested by Jay Dusard, comprised of a solution of 10.0 grams of sodium bisulfite in 1.0 liter of water.
- The fumes which emanate from acetic acid stop baths are perhaps the single greatest health hazard in the darkroom. Over time, these fumes can cause damage to the delicate membrane of the sinuses, resulting in respiratory problems. For this there are also two solutions.
  1. Use an odorless citric acid stop bath such as Kodak SB-8.
  2. Stop using stop baths altogether. Instead, substitute a one minute running water bath between the developer and fixer, for both film and paper. If running water is not available fill the tray or tank with fresh water, agitate for 20 to 30 seconds, dump, and repeat three times.

While a running water bath will not stop development as rapidly as an acid stop bath, it will slow it down to the point that the amount of residual development is insignificant. This is because, depending on its strength, it takes an acid stop bath approximately 15 seconds to halt development and a running water bath takes approximately 30 seconds. The difference in the negative image could not be measured. If you are still not convinced consider that the slight additional development will automatically be factored in when you run your film development test.

If you still prefer to use an acid stop bath instead of water the most widely used formulas call for acetic acid in a 1% to 2% working solution. The only other ingredient sometimes added is a pH indicator dye (Formulas: Stop and Hardening Baths: Indicator for Stop Baths).

Other chemicals that can be used to make stop baths are boric acid, citric acid, and sodium bisulfite. Chemicals that should not be used are chrome alum and potassium salts, such as potassium metabisulfite or potassium sulfite, either of which can cause green stains on some enlarging papers. In addition, the introduction of potassium salts into a fixing bath can convert the bath to potassium thiosulfate, which is nearly inactive as a fixing agent.[1]

FIXERS

In brief, the fixing process is the removal, after exposure and development, of unused silver halides, such as silver bromide, from the paper or film. This is necessary because unused silver bromide particles will eventually ruin the image. For this reason proper fixation is as important to the print-making process as proper development. Fixing can make the difference between an image of lasting value and an image that doesn't last.

The fixing process involves a series of chemical reactions in which the silver bromide is converted into complex argentothiosulfates, which are then dissolved by contact with fresh fixer and finally washed out of the film or paper. Upon immersing an emulsion (film or paper unless otherwise noted) into fixer, the first reaction is the conversion of unused silver bromide into an insoluble but not very stable compound. This compound can be seen by looking at negatives (not prints) after only a few seconds in the fix. They will appear milky in appearance. If fixation is not continued and the compound not completely dissolved, the negatives will rapidly degenerate.

As fixing progresses, the complex compound reacts with fresh hypo to form a soluble compound of *sodium* argentothiosulfate that can be removed by washing. In other words, fixing creates by-products; more fixing eliminates them. The actual rate of fixation is relatively fast. It is the breaking down of by-products (complex argentothiosulfates to soluble sodium argentothiosulfate) that takes time.

The fixing process for paper and film is similar, but film and paper have their own unique characteristics and requirements. Until the 1970s, the primary agent used for fixing was sodium thiosulfate (hypo). Other fixing agents, though not as common, include ammonium thiosulfate, alkali thiocyanate, thiosinamine, cyanide, sodium sulfite, ammonia, thiourea, and

[1] Prior to WWII, German companies formulated many stop baths using potassium salts, as they were less expensive than sodium (Germany was in a depression, as was the rest of the world). Subsequent research revealed the problems associated with potassium salts in stop baths and its use was discontinued. Unfortunately, there are still some old pre-WWII formulas floating around.

concentrated solution of potassium iodide. Except for special purposes (for example, ammonium thiocyanate can be used to achieve fixing times of a few seconds; Formulas: Fixers: Defender 9-F Rapid Thiocyanate Fixer), only two fixing agents are of interest to the general darkroom worker today, sodium thiosulfate and ammonium thiosulfate. Those fixers using ammonium thiosulfate are commonly referred to as "rapid fixers."

For practical purposes the difference between the two thiosulfates is a matter of fixing time. According to Pierre Glafkides, in *Photographic Chemistry, Vol. 1*, ammonium thiosulfate is 400% faster than sodium thiosulfate.[2] At some point, ammonium thiosulfate gained a reputation for producing less-than-permanent images. The problem was that ammonium thiosulfate, even in an undiluted concentrate, was not stable. Therefore, photographers desiring a more rapid rate of fixation would add ammonium chloride to their standard hypo solution just before use. This produced ammonium thiosulfate in solution.

Today, a stable form of ammonium thiosulfate is readily available in two forms. The preferred form is a 60% solution. However, when it is inconvenient to ship or store liquids, it is also available in photo-grade crystalline form. Although there are five published ammonium thiosulfate formulas, the two most used in contemporary photographic practice are ATF-1 and ATF-5.

Types of Fixer

There are three general types of fixing baths: plain (or neutral), acid, and alkali. A plain fixing bath is one consisting of hypo in water only. A plain bath can be easily mixed by adding two pounds of sodium thiosulfate crystals to one gallon of water. When using the crystalline form of sodium thiosulfate, begin with water of at least 90F/32C, as the temperature will drop considerably.

A plain hypo bath is often used prior to toning and sometimes as the second bath in a two-bath system. It has a short tray life and is not efficient at neutralizing alkali brought over from the developer. Used as the first bath with paper (Fixing Paper, below), or as the primary bath for film, a plain hypo bath may cause stains and other problems. For these reasons, it is not considered suitable for general applications or as a first bath.

Most fixers are of the acid type. Acid fixers are made by adding acid to the solution. Not just any acid can be used, as many would decompose the hypo and precipitate sulfur into the bath. Weak organic acids, like acetic acid, can be used, but only in combination with sodium sulfite in order to produce sulfurous acid in solution. Sulfurous acids can be used, but they are not stable in solution; sodium metabisulfite is more stable. Bisulfites can also be used and are more reliable.

Alkali fixers, especially those compounded with ammonium thiosulfate, are the most efficient and effective with modern emulsions in both film and paper. Although they have been used for scientific purposes since at least the 1930s, they have only recently become commercially available. Photographers' Formulary TF-4 is the first to be widely distributed. The formula for TF-3, a fixer having similar properties but a shorter shelf life, is given in the Formulas section.

[2]This may be overly optimistic as other sources suggest 200% to 300%. The point is, AT is considerably more efficient than sodium thiosulfate.

There are numerous advantages to using alkaline fixers.

- Shorter washing times. Paper fibers are akin to the fibers found in clothing; the reason laundry soaps are alkaline is because they wash out more readily from clothing fibers; there is no such thing as an "acid" laundry detergent or soap!
- No hypo clearing agent (HCA) is required when using alkali fixer.
- No acid stop bath is required when using alkali fixer. In order to preserve the alkalinity of the fixer, acid stop bath should not be used.
- Greater capacity than acid fixers.
- Both sodium thiosulfate and ammonium thiosulfate are more stable in an alkaline solution.

In addition to these advantages, keeping the process alkaline or neutral from developer to fixer will improve the permanence of the material as the thiosulfate will not mordant to the silver image or base.

Hardener

The purpose of hardener is meant to reduce the risk of injury to the emulsion of the film or paper while it is wet. This was of great importance when most film and paper were made with soft emulsions (Chapter 8, Printing Methods and Techniques: Hardener). After drying, hardener serves no useful purpose.

The reason not to use hardener is that it makes it more difficult for fresh fixer to penetrate the surface of the emulsion, and hardener is itself difficult to wash out of paper. The two most noticeable results are that fixing time is extended, even doubled, and some toners, such as selenium toner, will have an adverse reaction to hardener resulting in stains or uneven toning.

Even though most films made today are sufficiently hardened it is a good idea to include hardener in acid fixing baths for film, especially when processing sheet films in a tray. Roll film is mainly at risk when being removed from the reel for drying. Unless the fixer specifies not to use hardener (TF-4), the advantages of protecting film from scratches outweigh the disadvantages of using hardener.

For tray processing of paper it is not necessary to use hardener unless you habitually experience scratches on the print emulsion from handling. If scratches do occur, hardener should be added to the fixer. Start by adding one-third of the manufacturer's recommended amount and increase in one-third increments until the problem is eliminated. For example, if the directions call for 45.0 ml of hardener, start with 15.0 ml; if the problem persists, add another 15.0 ml. It will be necessary to neutralize or wash out the hardener prior to most toning processes (Formulas: Miscellaneous: De-hardener).

Chrome and potassium alum are the two most common hardening agents. Chrome alum has the greater effect, but fixers using this agent have poor keeping qualities. For this reason, potassium alum is usually preferred.

Fixing Negatives

A rule of thumb for fixing negatives is to allow at least twice the time required for the clearing of all traces of milkiness from the film. When the initial clearing time has doubled, as determined by periodic testing, it is time to mix a fresh fixing bath (see Determining Fixer Capacity, below).

Fixing Paper

The time-honored method for fixing paper, established by Kodak, is the two-bath method. In the two-bath method, two fresh fixing baths are placed side by side. Paper is immersed in the first bath for a predetermined time, drained, and moved to the second bath for the same amount of time. If the first bath is fresh, the paper is completely fixed and only trace amounts of fixing by-products are carried into the second bath. There the action of fresh fixer breaks down any residual by-products, which are easily removed during washing. As the first fixer begins to age, increasing amounts of by-product are carried over to the second bath and there eliminated.

The final step is the changing of the baths. After the first bath is exhausted, which is determined by one of the methods described in Determining Fixer Capacity, below, it is discarded and the second bath becomes the first. A fresh bath is mixed to replace the second. According to Kodak, after the third rotation both baths should be discarded and two fresh baths made. Agitation with this method should be at least 30 seconds every minute.

While not faulting this method, Ilford suggests the use of a single, concentrated, rapid fixing bath for 1 minute to prevent the buildup of by-products in the paper's emulsion. This method works because the paper is 90% to 100% fixed within the first 15 seconds of a concentrated fixing bath.

For this method to be effective it is important to monitor the time exactly. The paper should be immersed for 60 seconds with continuous agitation, drained for 15 seconds, and immediately transferred to a fresh water bath, preferably with running water. Excess time in the fixer beyond 60 seconds allows by-products to infiltrate the emulsion negating any advantage of the method.

Both methods have their merits, and neither appears to be better than the other. One advantage of the two-bath method is that whichever fixing agent you choose, sodium or ammonium thiosulfate, the fixing time is not as critical as in the single-bath method.

Agitation for Film and Paper

Agitation during fixation is critical for both film and paper. It is necessary for the complex argentothiosulfates to come into contact with fresh fixer in order to break them down. For film, agitation should be 30 seconds every minute.

Paper agitation depends on the method of fixation: Kodak Two-Bath or Ilford Single-Bath with Rapid Fixer (see Fixing Paper, above). If the two-bath method is used, agitate for 30 seconds each minute. If using the single-bath method, agitation should be continuous.

After one-quarter of the total fixing time has been reached, the film or paper can be exposed to light for examination. For example, if the total fixing time is 3 minutes the lights can be safely turned on anytime after 45 seconds.

Determining Fixer Capacity

Changing the fixer *before* it reaches exhaustion is critical for the longevity of photographic materials. Ammonium thiosulfate fixers will smell like ammonia when they are fresh, and sodium thiosulfate fixers should hardly smell at all. As a fixer reaches its useful capacity, it will begin to smell like sulfur. When the smell becomes strong, it is reaching its capacity.

Working dilutions of fixer should not be kept more than two months, less if the ambient temperature is over 85F/29C. Any fixer, whether stock or working dilution, should be discarded if it turns yellow or a white precipitate appears. This means that sulfur is precipitating out of the solution.

Both Film and Paper

There are two methods that can be used for testing either film or paper, and a third method for use with film. Use whichever works best for you.

- Every manufacturer publishes the capacity of its fixer which usually errs on the conservative side. Keep count of how many 80^2 inches of film or paper have been fixed. When the manufacturer's recommended limit has been reached the fixer should be discarded. If the capacity is not known a safe rule to follow would be 20 rolls of film or 8 × 10 inch sheets of paper per liter/quart (80 per 4.0 liters/gallon) with acid fixer and 25 with alkaline fixer.[3]
- Using a liquid hypo check (Formulas: Miscellaneous: Fixer Test Solution) is a reliable means to test fixer exhaustion but *only if you are accurate in your measurements and testing procedure*. The potassium iodide must be 10.0 ml of a 4% to 5% solution, and the amount of hypo tested should be exactly 100.0 ml. To create a precipitate, the combined solutions must be shaken; otherwise the test is prone to errors.

For Film

An alternative method for testing film fixer is to gently agitate an undeveloped piece of leader from a 35 mm or 120 roll of film in fresh fixer and time how long it takes to clear (become transparent). This should be done in normal room light. This will tell you two things: The minimum fixing time and if the fixer is exhausted.

The minimum fixing time is twice the time it takes the film to clear in fresh fixer. With some concentrated formulas such as Ilford Rapid Fixer or Photographers' Formulary TF-4 the film may be clear in 15 to 20 seconds. Even so, I recommend a minimum fixing time of 3 minutes for all films and fixers, except for those that are meant for extremely rapid fixing, such as Defender 9-F Thiocyanate Fixer. This is not a "scientific" recommendation—it is my recommendation. One extra minute or two of fixing time will not adversely affect the film and it will help insure complete fixation as the fixer ages.

By periodically testing the fixer, ideally before each fixing session, the exhaustion rate of the fixer can be determined. When the initial clearing time has doubled it is time to mix a fresh fixing bath. If you find it too difficult to remember to test the fixer before each session then check when the fixer is about half way through its estimated useful life and more frequently as it nears its published capacity.

It is a good idea to test a leader from each type of film you will be fixing as the clearing time will vary for different film types, with faster film taking longer to clear.

[3] Most fixers will last considerably longer than this recommendation. However, if not certain it is better to err on the side of caution.