A BETTER BLACK AND WHITE REVERSAL BLEACH WITH HYDROGEN PEROXIDE

DIY slides from most B&W films with a good performing peroxide bleach

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In a previous post, I described how to develop your own black and white slides using a simple bleach based on hydrogen peroxide and vinegar. This post is about an improved bleach that has a number of advantages over that one.

There are a lot of patents out there from the 1970s through the late 1990s covering peroxide bleaches for photography. Many of them claim excellent results. None of them that we tested produced those results. One assumes that they generally did not include the very best formula, but only enough to prevent others from using it. Some of us on Photrio tested a lot of them and worked for about 6 weeks straight to refine our knowledge to the point where we have a pretty good bleach.

Others have done work in this field in recent years and there are a couple of citric acid/peroxide bleaches that have been used. The first, and most notable is Ricardo Leite's.

However, most peroxide bleaches suffer from one or more of the following problems:

1. **Emulsion Damage** — Peroxide bleaches work by breaking down hydrogen peroxide to oxidize the silver. This necessarily releases free oxygen. In certain emulsions that free oxygen creates quite noticeable emulsion damage on the way out.
2. **Gold Staining** — Most peroxide bleaches we tested, including those mentioned above, result in staining, or unpredictably result in staining. This can leave a general gold tone to the slides, which may not be desirable.
3. **High Temperature** — Many peroxide formulas require high temperature, which may not be reasonable for many film stocks. It may also further damage the emulsion or shorten the life of the film once developed.
4. **Peroxide Strength** — Some recipes call for 9% or higher peroxide concentrations. This makes them not as desirable to handle and makes it harder for people in many parts of the world to source the ingredients. Most people who can obtain hydrogen peroxide can obtain 3% in various forms.
5. **Nasty Ingredients** — Some bleaches have required some unpleasant chemicals, such as silver nitrate or concentrated sulfuric acid.
6. **Unpredictable Performance** — Some bleaches significantly change in behavior over time, or while sitting overnight. This makes prescribing times for bleaching difficult.
7. **Fixing** — Acetic acid based bleaches seem to work as a reasonably strong blix and that results in lower Dmax than desired.

Experience with the vinegar bleach is that it does work well. However, it suffers from 1, 2, 3, 6, and 7 above. With certain films and very clean ingredients, it does work well! I wanted to get something that solved all of the above. We have not yet quite gotten there. What is proposed below solves issues 2-7. Issue 1 remains for certain films. Notably we have not yet got a peroxide bleach that works well with films that have a very hardened emulsion. Ironically both of the commercially available black and white slide films are in that category (ADOX Scala 160 and Fomapan R100). They are hardened because permanganate bleach softens the emulsion and they are usually used with that.

After a lot of testing, we settled on using two different chelating agents: ethylenediaminetetraacetic acid (EDTA) and citric acid. Both are fairly widely available and both are inexpensive. Neither poses much health risk. EDTA is not the best thing for the environment as it has been found to not break down well. However, it is widely used in cleaning products, detergents, and other chemistry that requires sequestering metallic compounds. It is normally used where tap water might be problematic. It is also used in medical treatment where someone has suffered from lead or other heavy metal poisoning.

Citric acid is the organic acid produced by citrus fruits! Lemon juice, lime juice, and the like contain citric acid. Here we are using the concentrated stuff, often available from health food stores or suppliers.

RECOMMENDED FILMS

Not all films work because of problem 1 above (emulsion damage). However, some films work very well. The following are known to work **well**:

- Fomapan 400
- Fomapan 100
- Ilford FP4
- ORWO N75

Known bad choices that do not work well:

- Agfa Scala
- ADOX Silvermax/Scala 160
- Fomapan R100

STEPS

Please follow the steps from the previous article for the whole reversal process. In place of that bleach, use this one.

- **Bleach —** 7 to 9 minutes by inspection in room light
- **Clearing Bath —** 1 minute 30 seconds to 2 minutes, continuous agitation

BLEACH FORMULA

Here is the recipe at which we've arrived, which solves problems 2-7 as described above:

- **Hydrogen Peroxide 3%** — 300ml
- **EDTA free acid powder** — 12g
- **Sodium Bicarbonate** — 19.5g
- **Citric Acid 99.95% crystals** — 11g

I was able to obtain the EDTA free acid here in Ireland. It may not be as available as some of the EDTA-sodium salts. You can substitute EDTA-2Na or EDTA-4Na salts. These are sometimes supplied in various hydrations. If using anhydrous the following should apply (thanks to Anon Ymous on Photrio):

- Disodium salt: use 13.8g EDTA-2Na, and only 12.6g sodium bicarbonate
- Tetrasodium salt: use 15.7g EDTA-4Na, and only 5.7g sodium bicarbonate

Mix in order. If using EDTA free acid, it will not dissolve until the bicarbonate is added, it has been stirred, and all the bubbling has died down. Except for this case, stir at each step and make sure everything is fully dissolved.

The target pH is about 4.5, which is critical to bleaching performance. This should bleach a roll of film in about 7 minutes at 20C, or 8 minutes at 17C. It is not very termperature sensitive, so should work at your "room temperature" in most cases.

If you mix this up and find that performance is not good, slowly increase the amount of citric acid until it becomes faster. The change is quite noticeable.

The final bleach should be clear until used, after which it will turn milky. After sitting, sodium citrate will precipitate on the bottom. You can use the bleach as is, or filter.

The bleach seems to keep well in a sealed jar, but peroxide breaks down in UV light, and so you should keep it in the dark or store in black or brown bottles.

Sodium hydroxide should work in place of the bicarbonate. I used bicarbonate because it's cheap, widely available, not hazardous, and I can obtain it easily. It is available in reasonably pure form in most supermarkets wherever you live.

OBTAINING INGREDIENTS

These are not quite supermarket chemicals like the previous bleach. However, they are not that hard to obtain, either.

- Citric acid is available from many health stores or suppliers. You want the powder/crystalline form as pure as you can get it. Mine is 99.95% pure.
- EDTA is available from chemical suppliers, suppliers of cleaning products, and other sources. Name brands include Dissolvine Z (note the "Z") and Versene. In Europe you should be able to obtain the 4Na/tetrasodium version from here if you are not able to get it closer to home.
- Sodium bicarbonate is available at any supermarket! This is just baking soda or "bread soda" depending on where you live. In the US you can just use Arm and Hammer. In Europe or elsewhere, just use your local brand.

CLEARING BATH

If you want to obtain the best clarity in your slides, you will need to follow the bleaching step with a sulfite clearing bath. This is common with other bleaches and is required here to get the best results. This is regular sodium sulfite that would be used in photography or as a preservative. You can obtain it from the normal suppliers of photo chemistry or from places like wine makers shops. You cannot substitute anything else that I know of. Sulfite is widely available and cheap so you should just use that.

Formula:

- **Water** — 800ml
- **Sodium sulfite** — 20g
- Water to 1L

Once bleaching is complete, you'll run the film through this clearing bath for 1 minute 30 seconds to 2 minutes with continuous agitation.

HOW IT WORKS

As is probably clear by now, I am not a chemist. But I have spent nearly a hundred hours reading patents, reading chemistry texts, and testing bleaches. The following is based on my understanding from having done so and from information I have been kindly given by folks on Photrio.

Hydrogen peroxide is a good oxidizer and silver is a catalyst in the break down of hydrogen peroxide. This means we can leverage the peroxide to oxidize the silver well. But simply oxidizing it is not enough, we need to get the oxidized silver to combine with another agent, one that will form a complex with it that is either soluble in the bleach, or soluble in a compatible clearing bath.

Adding enough EDTA by itself to a peroxide bleach does work on its own. However, it leaves a general gold stain across the frame, one that does not dissolve in the clearing baths we tried. This appears to be large grains of silver that redeposit onto the emulsion. And it uses a LOT of EDTA.

It turns out that adding enough citric acid to the bleach allows it to complex with the silver that was otherwise formed into large grains by the EDTA and that formed the gold staining. With citric acid in the bleach, silver citrate is instead formed, and precipitates either into the emulsion or out of the solution on the bottom of the tank. Silver citrate is not very soluble in water.

Silver citrate is light sensitive and if not removed from the emulsion, will develop and darken in the second developer. Using the sulfite clearing bath allows the silver citrate to be dissolved from inside the emulsion and into the clearing solution.

If you are interested in more examples of bleaches, relevant patents, and various experimental attempts, feel free to follow the many pages of posts in the thread linked at the beginning.

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