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DEVELOPERS, AN INTRODUCTION

Introduction

Is it important to know about most technical things in photography? I am not by nature a technical person and I believe that for the most part it is not important. While it may be intellectually interesting about things like hyperfocal distance and the Scheimpflug principle or the relative merits of different lenses, knowing these things will not make you a better photographer, just as knowing how an internal combustion engine works will not make you a better driver.

In 1970 I taught a class at the Philadelphia College of Art (now, University of the Arts) called “Theory and Technique.” Since I was a self-taught photographer, I knew virtually none of what I had been hired to teach before the semester began, though I had told them I did. I spent the entire semester studying, not making even one photograph during that time. Each week I studied from between four and fifteen books, trying to understand the material, which was not always easy for me, and then prepared the two-hour lecture for that week.

I had one student in my class with an engineering degree from Carnegie Tech who now was in art school after having decided that he did not want to be an engineer. It seemed that he knew twice as much as I did and I really needed to be on my toes. At the end of the semester after the final exam he asked me if I had gone to R.I.T. Inwardly, I did the equivalent of pumping my fist in the air.

Now, over thirty years later, I remember almost none of what I taught during that semester, nor have I needed to remember it. Almost all of it is irrelevant to making pictures, which is what I assume everyone who uses a camera wants to do. Long ago I came to the conclusion that there is only one technical thing in photography that is essential to know—the exposure/development relationship. And you must know that as automatically as counting from one to ten. I am constantly amazed at how many budding photographers cannot instantly tell whether a thin negative is underexposed and/or underdeveloped, or whether a denser one is over exposed and/or overdeveloped.

There is one other thing that, while not essential, is useful to know, and that is about the constituents of developer solutions. Knowing this enables you to modify the developers you use, allowing you to better control the development process of both negatives and prints, thereby affecting the final look of your photographs. What follows is a primer on developers.

The Constituents of Developer Solutions

Developers generally consist of four kinds of chemicals:

- The Developing Agent
- The Preservative
- The Accelerator or Alkali
- The Restrainer
- Occasionally, other chemicals, mainly buffers, are added.

The action of any developer is a function of how each of these kinds of chemicals is combined. Many developing formulas have the same chemicals in them, but by varying the proportions, widely varying results can be achieved.

The Developing Agent:

The process of development is a process of chemical reduction. The easiest way to understand this is to think of reduction as being a process whereby compounds are changed back (reduced) to their constituent elements. During the development process the developing agent reduces the silver halide, which is what a sensitized emulsion is, to metallic silver. There are many chemicals that act as reducing agents that are capable of reducing silver halide to metallic silver, but for photographic use only those agents that discriminate between the exposed silver halide and that which was not exposed are used. It should be obvious that an agent that reduced all of the silver halide to silver would be useless for photographic purposes. The developing agent can, in part, determine effective film speed, extent of graininess, sharpness, and contrast.

The Preservative:

During the developing (reducing) process, the developing agent becomes oxidized. So that the development process remains constant throughout, a preservative must be added to prevent this oxidation. If it were not, the developer would quickly become exhausted.

The Accelerator:

Most developing agents require an alkaline environment in order to be effective and alkalis are added to raise the pH. The higher the pH, the faster and more active the developer is.

The Restrainer:

At the same time that the alkali is facilitating and speeding up development, a restrainer must be used to slow down the process, otherwise parts of the emulsion that did not receive exposure to the light might get developed. When this happens it is known as chemical fog.

Because the developing agents are affected by the other constituents of the developer solution, I will discuss them first.

Preservative:

Sodium Sulfite is almost always used as the preservative for the developing agent. A stated above, preservatives keep the developing agent from oxidizing, allowing development to proceed at an even pace throughout the whole of the developing time. When a great deal of sodium sulfite is added to the formula it raises the pH and acts as a mild accelerator. If it is used in sufficient quantity, it is possible to do without the accelerator. And in sufficient quantity it is also a silver halide solvent and therefore a large amount of sulfite is one of the constituents of fine-grain developers. There are a few formulas for fine-grain developers that use no alkali at all, only a great deal of sodium sulfite.

The Accelerator or the Alkali:

Development generally takes place in an alkaline environment. The higher the pH of the developing solution, the faster development occurs. When film is developed, not only is development speeded up with a higher pH, but grain size gets larger. The lower the pH, the smaller the grain. The most commonly found alkali in developers is sodium carbonate. It has a pH of around 11.5 – 11.6 and is used in most print developers. Potassium metaborate, essentially the chemical that the Eastman Kodak company marketed under the name Kodalk, has a pH of approximately 9.9. And borax, found in D-76, a fine-grain developer, has a pH of 9.5. Keep in mind that each whole number on the pH scale represents a difference of 10 times and that a pH of 7.0 is neutral—neither acid nor alkaline. Sodium carbonate is therefore 100 times more alkaline than borax. High contrast developers use caustic alkalis, such as sodium hydroxide, (pH of 12.0 – 14.0). When they are used, development is rapid and few mid-tones result.

The Restrainer:

The most commonly used restrainer is potassium bromide. Its function is to make sure that only the part of the film or paper that was exposed gets developed. It also slows the rate of development. Other restrainers occasionally used are the organic compounds, benzotriazole (Kodak Anti-Fog #1) and nitrobenzimidazole (Kodak Anti-Fog #2). They are quite powerful and are used in very small quantities.

Buffers and Other Additions to the Developing Solution:

Occasionally, sodium bisulfite (sodium metabisulfite is essentially the same chemical) is used as a buffer to enhance the preservative action of the sodium sulfite. Whereas sodium sulfite is weakly alkaline, sodium bisulfite is distinctly acidic. It is used when the developing agent is particularly susceptible to oxidizing, as is Pyro. When it is used, a greater degree of alkalinity (higher pH) in the working solution must be present. If the water used for developing film is excessively hard, EDTA (ethylenediamine tetra acetic acid) is sometimes used.

Developing Agents:

The two most frequently encountered developing agents are Metol and Hydroquinone. Others include Pyrogallol (Pyro), Glycin, Pyrocatechin, Phenidone, Para-Aminophenol, Paraphenylenediamine, and Amidol.

Developing agents can be measured by their reduction potential—how active they are. Metol has a reduction potential of 20. Hydroquinone has a reduction potential of only 1. Pyrogallol has a reduction potential of 16, and Amidol, the most active developer of all, has a reduction potential of 40.

When two developers are used together in the same solution and enhance each other they are exhibiting superadditivity.This is when the combined reduction potential of the developer exceeds the sum of the reduction potential of each developer working separately. Metol and Hydroquinone used together exhibit superadditivity. When combined, their reduction potential is significantly higher than 21, although I have been unable to find an exact number.

Developing agents also exhibit varying induction periods—the time it takes for the developing process to become visible and to really get going. Those developers that have a short induction period develop to a low contrast, while those that have a long induction period develop to a higher contrast. Metol develops quickly, but to low contrast and it is good at building shadow detail. Hydroquinone develops very slowly, but to a high contrast, and is not good for developing shadow detail. But when Metol and Hydroquinone are combined the result is a fast acting developer that develops to a fairly high contrast, but with the mid-tones and the shadows filled in. To see this, develop an exposed sheet of paper in Metol alone. The image will come up quickly, but will be gray and muddy. Now develop in Hydroquinone alone. It will take many minutes for any image at all to appear, but when it does it will be of high contrast.

Other information about specific developing agents:

Metol is readily soluble in water but not in a sulfite solution. When mixing all other developers you must first dissolve the sulfite, but not with Metol. It is only slightly effected by low temperature and reacts well with carbonate. When used for developing prints it gives warm tones.

Hydroquinone, unlike Metol, is considerably affected by low temperature. It gives cool tones when used for developing prints.

Phenidone is often used as a hypo-allergenic substitute for Metol. With used as a print developer it gives cool tones.

Pyrogallol is a staining developer used with films. The concentration of the preservative, the sodium sulfite, determines the stain. For most consistent results when using Pyro, mix the sulfite shortly before use because its storage life is shorter than that of the other components.

Amidol is the only developer that does not need an alkaline environment in which to work. It is generally a neutral-tone developer used for prints, but it can also be used to develop film. Because it can work in the absence of alkali, thereby avoiding the swelling of the emulsion that takes place when other developers are used, it can be used as a tropical or high-temperature film developer.

Pyrocatechin, like pyrogallol, is a staining developer and is used to develop film. Its use is generally restricted to those situations where it is necessary to preserve extreme high value separations. It is little used today.

Glycin is used as a very warm-tone print developer. It oxidizes slowly and gives a fine neutral toned image. Ansco 130 is the most common formula that used Glycin.

Para-Aminophenol is used as the developing agent in the film developer, Rodinal. has good keeping properties— in concentrated solution it does not readily oxidize. It is used in highly dilute concentrations and is not greatly affected by changes in temperature.

Paraphenylenediamine is used as a very fine-grain film developer, but it is slow acting and causes a loss of film speed, and it is highly toxic. I do not believe it is used much today.

Now that we know this information—how can we use it?

All formulas for the commercially available developers evolved over time and have withstood a great deal of experimentation. Nonetheless, knowing the constituents of developing solutions and what they do allows you to fine-tune the solutions to more precisely achieve the desired results. Increasingly today, after a lull of about fifty years, we see many photographers mixing their own developers. These developers are usually variations of published formulas, rather than something entirely new, but through their use results are achieved that are not possible any other way.

Dilution:

The easiest way to modify a developing solution is through its dilution. More dilute solutions work more slowly and to lesser contrast. More concentrated solutions develop more quickly and to a higher contrast. Dektol (a slight variation of the published formula Kodak D-72) is usually used 2 parts water to 1 part developer. But to get more contrast it can be used 1:1 and to get less it can be used 3:1.

The standard dilution for ABC Pyro is 1-1-1-7 (one part A, one part B, one part C, and seven parts water). Edward Weston used it in an extremely dilute form: 3-1-1-30. As a result, developing times were long, but he was able to achieve bright highlights without blocking. I develop my negatives in Pyro 1-1-1-7, but for extremely contrasty subjects, I use it 2-1-1-15. Using it 3-1-1-30 seems to result in developing times that are inordinately long, unless you cut the film speed by two or three times when making exposures.

Modifying the developing agent:

If you look at the published formulas for D-76 and D-72, you will find that except for the alkali they are virtually the same developer. Essentially, the same chemicals are used, just in different proportions. Both use Metol and Hydroquinone as the reducing agents as do most other published developing formulas. By varying the proportions of Metol and Hydroquinone a developer can yield low contrast (more Metol, less Hydroquinone) or one that can yield high contrast (less metol, more hydroquinone). Use of the two-solution Beers formula, which combined a Metol developer (solution A) with a Hydroquinone developer (solution B) in varying proportions enables one to achieve a whole range of contrast with one paper grade.

Modifying the accelerator or alkali:

When using ABC Pyro developer, the developer of choice for those developing film by inspection, a subject that I wrote about in a previous article (*View Camera,* May/June, 1999), it is possible to increase the contrast when development has gone to or past the normal development time, and when the negative still appears too thin. Not only can one choose to further extend development time, but additional sodium carbonate can be added to speed up development and add contrast. I do this often when I have photographed very flat scenes and when, after development is half or three quarters complete, it appears that a greatly extended developing time will be needed to give sufficient contrast. On the other hand, when photographing contrasty scenes one can cut the carbonate to insure that the highlights do not block up. Edward Weston used to cut the carbonate to less than half for his negatives.

Modifying the restrainer:

This is done mostly when printing. Adding additional potassium bromide or benzotriazole (I do not know of anyone who currently uses nitrobenzimiazole) when making prints will help keep the whites clear and therefore give a slight increase in contrast. Additional bromide will tend to make the print color slightly more greenish and additional benzotriazole will make the print color slightly more bluish.

Conclusion

Knowing the constituents of developing solutions and what they do allows you to modify them to fine-tune results. Who knows, with some experimentation, you may make a modification to the developing solution that will be useful to many other photographers. As a result, one day a developer may even have your name on it.

For those wanting to experiment with mixing and modifying your own developers, the best place to begin is Steve Anchell's *The Darkroom Cookbook* and the companion book *The Film Developing Cookbook*. They have many formulas to get you started. As an alternative, try to locate a copy of the old *Photo-Lab Index* that was published by Morgan & Morgan.