Photographic Chemistry

An introduction for the non-chemist

Traditional photography combines art, technology and science, predominantly chemistry. From preparing light-sensitive emulsions to developing and creating permanent images, photographic chemistry is the backbone of traditional photography, controlling exposure, development and fixation.

During the exposure, light is directed onto the emulsion, where its radiation affects light-sensitive silver salts and produces a latent image. A chemical treatment, called development, turns the latent image into a visible image, by converting the silver salts that were affected by the exposure into metallic silver. All remaining silver salts, not affected by the exposure and, consequently, not changed by the developer, must subsequently be removed to produce a permanent image. This is accomplished through another chemical treatment, called fixing, which is followed by a final wash in plain water to remove chemical residue.

A thorough understanding of chemistry is not required to effectively operate a darkroom. One can successfully process film and paper, using commercially available photographic chemistry, by simply following the instructions, without ever giving the underlying chemical processes much thought. However, preparing your own processing solutions according to a chemical formula, using raw chemicals, makes you independent of commercial product availability and provides the opportunity for customized process optimizations. In the following chapter, you will find a basic set of formulae for developers, a stop bath, fixers and other processing chemicals. To better understand the purpose and function of their main ingredients, it will be beneficial to have a rudimentary understanding of photographic chemistry.

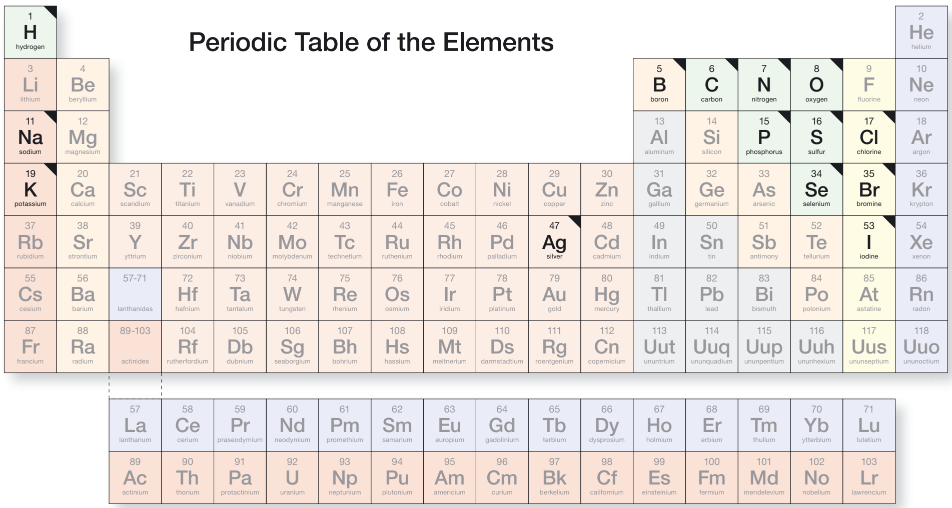

fig.1 As of this writing, in 2010, there are 118 elements known to exist, but only a few of them find significant use in silver-based photography.

Elements and Compounds

For much of its history, chemistry was a relatively simple science with all matter divided into just four elementary materials: air, water, earth and fire. This changed in 1661 when Robert Boyle summarized a better understanding of matter and proposed that there is a difference between elements and compounds. Since then, an element is defined as the simplest form of matter (atom), indivisible and with individual characteristics, but, combined with each other, elements can create a number of compounds (molecules) with distinctively different properties. As of this writing, there are 118 known elements (fig.1), but only the first 94 elements occur naturally on earth. The rest are mainly short-lived by-products of nuclear reactions. The number of possible compounds, on the other hand, seems to be endless.

Compounds, created by chemical reaction, often have properties quite different from the elements they are made of. For example, the elements sodium and chlorine are both extremely dangerous, but when combined chemically, they produce harmless sodium chloride, which we know as ordinary table salt. The chemical equation for this reaction is written as:

$$Na + Cl = NaCl$$

sodium + chlorine = sodium chloride

Types of Compounds

Elements can be roughly divided into two groups: metals and non-metals. Compounds can be classified as being organic or inorganic. Organic compounds are mainly composed of hydrogen, carbon, nitrogen, oxygen and sulfur. Inorganic compounds usually contain metallic elements. Another useful classification of compounds (fig.2) differentiates four groups:

Oxides are compounds of oxygen and other elements. Examples are sulfur dioxide ($S + O_2 = SO_2$) and sodium oxide ($4Na + O_2 = 2Na_2O$). Many oxides are soluble in water, and, depending on the type of element combined with the oxygen, this results in either an acid or a base.

Acids are formed when the oxides of non-metallic elements are dissolved in water. For example, sulfur dioxide dissolved in water produces sulfurous acid ($SO_2 + H_2O = H_2SO_3$). Acids are sour and have a pH value < 7.

Bases are formed when oxides of metallic elements are dissolved in water. For example, sodium oxide dissolved in water produces sodium hydroxide ($Na_2O + H_2O = 2NaOH$). Bases are alkaline and have a pH > 7.

Salts are typically combinations of acids and bases. For example, when sulfurous acid reacts with sodium hydroxide, sodium sulfite is formed ($H_2SO_3 + 2NaOH = Na_2SO_3 + 2H_2O$). Sodium sulfite is found in many photographic formulae.

pH

The 'power of hydrogen', or pH, is a measure of strength for an acid or alkaline solution (fig.3), and measured pH values typically range from 1 to 14. Roughly speaking, the pH value is the negative logarithm of the hydrogen ion concentration, but it is more important to remember that acids have pH values < 7 and bases have pH values > 7. Distilled water is said to be neutral with a pH of 7.

Precise pH measurements require sophisticated pH meters, but sufficiently accurate pH values can be obtained with a litmus test. Litmus is a water-soluble dye that changes its color depending on the pH value of the solution with which it comes into contact. Test papers, containing litmus, turn bright red in acid solution and deep blue in alkaline solutions. The actual pH value can be estimated by comparing the resulting color to a calibrated color chart.

A pH test is useful for darkroom workers, because the pH value of a photographic solution is often an indicator of its freshness or activity. For example, a fresh acid stop bath has a pH value of 4 or less, but when in use, it will be continuously contaminated with alkaline developers. The alkali carry-over raises the pH value of the stop bath, and by the time it approaches a pH value of 6, the stop bath has lost most of its usefulness and must be replaced. In another example, the pH value of a developer can be an indicator of its activity. A changing pH value, due to age or usage, will lead to process inconsistencies, which can be predicted and controlled, after the actual pH value has been determined.

Chemistry and Photography

In 1727, Johann Heinrich Schulze experimented with several compounds of silver and noticed that silver salts darkened under the influence of light. In 1802, Thomas Wedgwood and Humphrey Davy coated paper with a silver-salt solution and exposed it in a camera obscura to produce an image, which could only be seen for a limited time. In 1834, William Henry Fox Talbot suggested that a developer could amplify a weak exposure of silver salts, turning a latent image into a visible image, and in 1837, two years prior to the official invention of photography, John Herschel proposed sodium thiosulfate as a solvent for unexposed silver salts to create a permanent image.

Emulsion

A photographic emulsion is a thin layer of light-sensitive material suspended in photography-grade gelatin. The gelatin makes it possible for the emulsion to be coated onto a substrate of glass, plastic film or paper. Three silver salts have been found to be particularly sensitive to light: *silver chloride* (AgCl), *silver bromide* (AgBr) and *silver iodide* (AgI), and as a group, they are often referred to as silver halides.

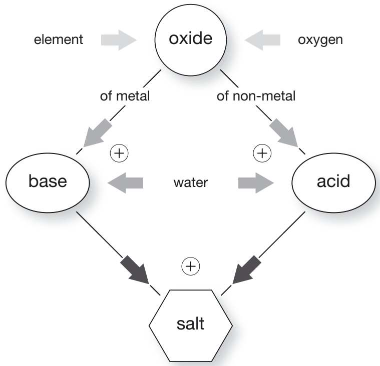

fig.2 Chemical compounds can be divided into oxides, acids, bases and salts.

pH	
14	
13	
12	
11	*alkalinity*
10	
9	
8	
7	*neutral*
6	
5	
4	*acidity*
3	
2	
1	

fig.3 The pH value is a measure of how strong an acid or alkaline solution is.

Typical emulsions contain a mixture of two or three silver halides, because they differ in light and color sensitivity. But, even as a group, they are mostly blue-sensitive and not able to record the entire visible spectrum. To make silver halides responsive to all wavelengths of light, complex organic chemicals, so-called optical sensitizers, are added to the emulsion. They act as an internal color filter, extending the color sensitivity from blue into green and red.

During the exposure, light energy is absorbed by the silver-halide crystals, which produces a chemical reaction within the salts. This creates a latent image, which is made visible through development.

Developer

Developers are able to differentiate between exposed and unexposed silver halides. They liberate exposed silver halides from their salts and reduce them to metallic silver, but unexposed halides remain untouched. The chemical process of development is rather complex, and an exact equation cannot be given, but in simple terms, the following reaction takes place:

$$\begin{matrix} AgCl \\ AgBr \\ AgI \end{matrix} > \text{exposure} > \text{development} = Ag$$

Developer solutions contain a number of ingredients, which can be divided into four groups:

Developing Agents are relatively complex organic compounds, which provide the electrons required to reduce silver ions to metallic silver. The most commonly used developing agents are *metol*, *hydroquinone* and *phenidone*.

Accelerators increase the alkalinity of the developer and provide additional ions to create metallic silver. In general, the higher the pH value of the developer, the more active it is. Typical accelerators are *sodium hydroxide*, *sodium carbonate* and *borax*.

Preservatives are added to developer solutions to protect developing agents against oxidation. A frequently used preservative is s*odium sulfite*.

Restrainers suppress the formation of chemical fog, which is an unwanted silver production on unexposed silver halides. A minute amount of *potassium bromide* effectively reduces fog, but larger amounts affect the rate of normal development.

Stop Bath

Once the desired degree of development has been reached, the process must be stopped quickly to avoid overdevelopment. This can be achieved through a simple water rinse, but an acid stop bath is more effective in neutralizing the alkaline activators and stopping development almost instantaneously.

A dilute solution of *acetic* or *citric acid* makes for a powerful stop bath. However, with developers containing *sodium carbonate*, the acid concentration must be kept sufficiently low to avoid the formation of carbon-dioxide gas bubbles in the emulsion, because this may lead to 'pinholes' in the emulsion.

Fixer

After the stop bath has successfully terminated the development of exposed silver halides, all unexposed halides still remain in the emulsion, because they are not soluble in water. This is of great benefit during the development process, but during fixing, they must be removed completely, or they will eventually darken upon further exposure to light, and the image will not be permanent. This requires a fixing bath with a number of ingredients:

Fixation Agents must dissolve all remaining silver halides and convert them into water-soluble compounds. Only two chemicals, *sodium* and *ammonium thiosulfate,* are known to do that without negatively affecting the silver image or the gelatin layer. Since *ammonium thiosulfate* dissolves silver halides more rapidly than *sodium thiosulfate,* it is commonly known as 'rapid fixer'.

Acids are optional fixer ingredients, separating fixers into acid and alkali solutions. Acid fixers have the benefit of neutralizing any residual developer solution and preventing emulsion swelling in the wash. Often, a combination of *acetic* and *boric acid* is used. Acid-free fixers produce a less objectionable odor and are easier to wash out of the emulsion.

Preservatives are used with acid fixers to prevent an accumulation of sulfur, due to a reaction of thiosulfate with acids. This is achieved by adding *sodium sulfite*, which quickly reacts with colloidal sulfur and creates fresh sodium thiosulfate.

Hardeners can be added to prevent excessive swelling of the emulsion during washing and protect against physical damage. The most widely used

> I have never considered myself to be technical. To me, adding bromide or carbonate to a developer is about as technical as exposing for the shadows. Every photographer should know that!
>
> Steve Anchell

hardener is *potassium alum*. Hardeners impede washing and are not recommended for normal processing, but they find use in special application. **Buffers** such as *sodium sulfite* and *sodium carbonate* are used to stabilize the pH value of acid and alkali fixers. If alkali fixers are preceded by an acid stop bath, *sodium carbonate* must be substituted with *sodium metaborate* or *balanced alkali* to avoid the formation of carbon-dioxide gas bubbles.

Washing Aid

After fixing, emulsion and film or print substrate contain a considerable amount of thiosulfate, which must be removed so not to adversely affect later processing operations and to optimize image longevity. Washing is a combination of displacement and diffusion, and consequently not a chemical but a physical process. However, certain chemicals can positively affect the rate of washing and its efficiency.

According to *Modern Photographic Processing* by Grant Haist, a salt bath prior to washing was suggested as early as 1889, and washing in seawater has been known to speed up the rate of washing since 1903. On a global average, seawater contains roughly 3.5% salt, mainly sodium chloride. Unfortunately, seawater cannot be left in the emulsion, because the remaining salts cause a fading of the silver image under storage conditions of high humidity and temperature.

The modern alternative to seawater is a washing aid, containing up to 2% of *sodium sulfite*. Applying a washing-aid bath prior to the final wash is standard practice with fiber-base print processing, and is also recommended for film processing. It makes residual fixer and its by-products more soluble and reduces the washing time significantly. Washing aids are not to be confused with hypo eliminators, which are no longer recommended, since recent research has shown that minute amounts of thiosulfate actually protect the silver image against environmental attack.

An alternative to using *sodium sulfite* alone is using it together with *sodium bisulfite*, which is done in commercial washing aids. This constitutes a compromise, as lower pH values reduce emulsion swelling in the wash, but lowering the alkalinity also reduces the rate of thiosulfate elimination. To prevent calcium precipitation and 'print scum', some *sodium hexametaphosphate*, also known as *Photo Calgon*, may be added to the washing aid as a sequestering agent.

Toner

Unprotected metallic image silver is subjected to constant attacks by reducing and oxidizing agents in our environment. The mechanisms of image protection are not entirely understood, but the positive influence of *sulfide* and *selenium* on silver image permanence is certain. Toning baths, containing *sodium sulfide, polysulfide* or *selenium*, convert the image forming metallic silver into more stable silver compounds, such as silver sulfide and silver selenide, and *sodium carbonate* buffers the pH value in polysulfide toners.

The information presented in this chapter was not designed to withstand scientific scrutiny. Instead, it was purposely oversimplified to provide a brief overview and basic understanding of chemistry and photographic processes, while trying to avoid getting hopelessly lost in scientific detail. I trust this will make some more comfortable with photographic chemistry and instigate others to deepen their studies. Much of what has been presented here can be found in far more detail in an excellent book, called *Photographic Chemistry* by George T. Eaton, which is unfortunately out of print. I highly recommend finding a secondhand copy of this book to anybody interested in the subject of photographic chemistry.

A Note on Mixing Chemicals

The sequence in which chemical compounds are listed in photographic formulae is not accidental. Always add them one after the other, according to the list.

a. weigh out dry chemicals onto separate pieces of small paper
b. arrange chemicals in order and add them one after the other
c. slowly sift chemicals into water while steadily stirring it
d. make sure it is completely dissolved before adding the next
e. always add acids to water and never the reverse, or spattering may cause serious injury
f. add alkali and acids slowly, as they may create intense heat when dissolved or diluted

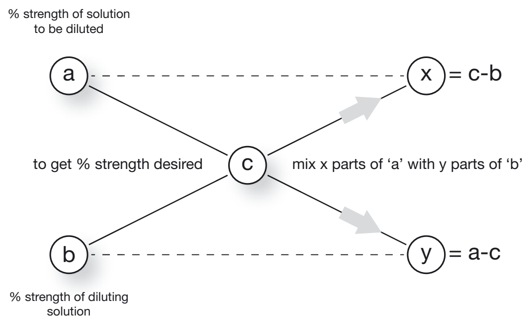

fig.4a The crisscross method is a simple technique of mixing two compatible liquids into a target solution of desired strength. It can be used to create a working solution from two existing stock solutions, or it may help to determine how a stock solution must be diluted to create the working solution.

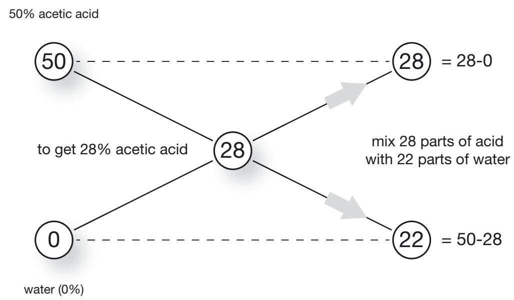

fig.4b In this example, 50% acetic acid is mixed with water (0%) at a ratio of 28/22 to create 28% acetic acid, by subtracting the working strength (c=28) from the stock strength (a=50) and the diluting strength (b=0) from the working strength (c=28) and knowing how many parts of each are required for the mixture.