CHEMISTRY OF PHOTOGRAPHIC PROCESSING

A camera has been called a "magic box." Why? Because the box captures an image that can be made permanent. Photographic chemistry explains how this happens and this instruction sheet is a presentation of basic photographic chemistry.

THE EMULSION

The first magical part of photographic chemistry is the photographic emulsion. As you recall, film is made up of a support and an emulsion. The emulsion has two major ingredients: *Silver Halide Crystals* and *Gelatin*. The silver halide crystals capture the photographic image. The gelatin holds the silver halide crystals in place, somewhat like Jello holds pieces of banana in place.

The silver halide crystals are more important than the gelatin in an emulsion because they are light sensitive. The photographic image formed when light strikes the silver halide crystals is invisible or *latent*.

Photographic processing chemicals make the latent image formed by the light sensitive halide crystals *visible* and *permanent*.

GENERAL CHEMISTRY FACTS

To learn how photographic processing chemicals make latent images visible and permanent, it is necessary to learn some general facts of chemistry.

ELEMENTS

Chemically, everything in the universe is made up of about 100 different elements. An element is the simplest kind of matter because it contains atoms of only one kind. As an example, oxygen is an element because it contains only one kind of atom. In addition, silver has only one kind of atom, so silver is also an element.

We can divide elements into two classes: metallic and non-metallic. Silver is a metallic element. The table below shows elements of interest to photography and whether they are metallic or non-metallic.

ELEMENTS

METALS		NON METALS	
Sodium	Silver	Carbon	GASES:
Potassium	Gold	Boron	Hydrogen
Calcium	Platinum	Sulfur	Nitrogen
Iron	Aluminum	Iodine	Oxygen
Copper	Mercury	Bromine	Chlorine

COMPOUNDS

When two or more elements react together, they form a type of matter unlike the elements. This type of matter is called a *compound*. For example, two elements, hydrogen and oxygen, combine to form water (H_2O). Water, then, is a compound. Two atoms of hydrogen combine with one atom of oxygen to form H_2O. This makes three atoms, but there are only two kinds of atoms present. When two or more elements react to form a compound, the chemical reaction is called *composition*.

ORGANIC AND INORGANIC COMPOUNDS

Just as there are two classes of elements, metallic and non-metallic, there are two classes of compounds: organic and inorganic. Organic compounds are associated with living things, plant or animal. Inorganic compounds are associated with things not living. For example, the gelatin used in film emulsions is a compound made from the hides and bones of cattle, so gelatin is an organic compound. The principle elements contained in many organic compounds are: carbon, hydrogen, nitrogen, and sulfur. Only one element, carbon, is contained in ALL organic compounds. Thus, gelatin, because it is organic, must contain carbon.

Inorganic compounds never contain carbon. Water is made up of only Hydrogen and Oxygen and contains NO carbon. Therefore, water is inorganic. Inorganic compounds often, but not always, contain metallic elements such as silver, potassium or sodium. Silver halides are compounds that contain silver, but do not contain carbon. Therefore, they are inorganic.

OXIDES

Oxides form a group of chemical compounds that are very important to photographic processing. An oxide is a compound formed of oxygen and another element. Oxygen is non-metallic, but it can combine with either metallic or non-metallic elements and both are called oxides.

Some oxides can be dissolved in water. When an oxide formed of oxygen and a non-metallic element is dissolved in water, an *acid* is formed. Acids, therefore, are related to non-metallic elements.

When an oxide formed by oxygen and a metallic element is dissolved in water, a *base*, or *alkali*, is formed. Alkalines are, then, related to metallic elements.

The easiest way to tell an acid from a base is to use litmus paper. When litmus paper is dipped into a liquid, it turns color. An acid turns litmus paper red while a base turns it blue.

An acid and a base can react together to form two new compounds: water and a salt. Water is always a product of the reaction between a base and an acid. The *type* of salt formed by the reaction depends upon the elements found in both original compounds. Salts formed by this reaction can be either acidic, basic, or neutral. The water is, of course, always neutral. If litmus paper is placed into a solution of salt and water and it turns red, the salt is an acid. If it turns blue, the salt is a base.

The amount of acidity or alkalinity of a solution is measured by the pH scale. The pH scale consists of numbers 0-14. 0-6 are acids; 7 is neutral (water); 8-14 are bases. The farther away from 7, the more acid or alkaline the solution is. Thus, an acid of 3 is stronger than an acid of 5; a base of 12 is stronger than 9.

Acids	Bases	Salts
Acetic Acid	Sodium hydroxide	Sodium sulfite
Hydrochloric Acid	Sodium Carbonate	Sodium sulfate
Sulfuric Acid	Kodalk Balanced Alkali	Potassium bromide
	Borax	Sodium Thiosulfate
		Potassium Alum
		Chrome Alum

BASIC PHOTOGRAPHIC PROCESSING CHEMISTRY

Acids, Bases and Salts are all used in photographic processing solutions. The oxides are used to make acids, bases and salts but are never used directly in photographic processing.

Acids are used in stop bath and fixing solutions. Therefore, they have pH values less than 7. Bases are used in the developer. Thus, developers have pH values greater than 7.

Salts, which can be acid, neutral or base, are used in developers and in fixing baths. Sodium thiosulfate, a salt, is the main ingredient in fixer. Potassium Bromide, often found in developer, is also a salt.

With the exception of acetic acid (stop bath), most of the bases, salts and acids used in photographic processing are inorganic, and, thus, contain no carbon.

Water, also inorganic, is used in *all* photographic processing solutions. The water acts as a *solvent.* That is, it is used to dissolve the other compounds used in processing chemicals so that the chemicals can do their work on the emulsion of the film. It is also used to remove any left-over chemicals remaining on the emulsion during the wash step.

Some important organic (carbon-based) compounds are also used in photographic processing. The developing agent in developer is an organic compound and, thus, contains carbon.

MAKING AN IMAGE VISIBLE AND PERMANENT

DEVELOPER

Photographic processing solutions make the latent image visible and permanent. It must be made visible before it can be made permanent. Developer is used to make the latent image visible.

The developer must contain certain kinds of chemical compounds, although the amounts and actual compounds used may vary from developer to developer. Developer is a solution, therefore a solvent (water) is used to dissolve the chemicals before they can work.

DEVELOPING AGENT

The most important compound in a developer is the developing agent, an organic compound which actually makes the latent image visible. (Most developing agents are chemically related to benzene, which contains carbon and hydrogen. Because the developing agent contains carbon, it must be an organic substance.) *Hydroquinone*, an organic compound, is a popular developing agent often found in developing solutions.

In order to make the latent image visible, the developing agent acts upon the exposed light-sensitive silver-halide crystals. Each exposed silver halide crystal contains an invisible speck of metallic silver, while unexposed crystals contain no such specks. A developing agent acts upon each crystal containing a speck of metallic silver and turns the entire crystal black. When all the exposed light-sensitive crystals have turned black, the image is visible. Because unexposed crystals contain no specks of metallic silver, the developing agent does not cause them to turn black.

If developing agents did their job perfectly, there would be no need for any other compounds in the developer. Water and one or two developing agents would make up a developing solution. However, developing agents are imperfect and other compounds must be added to help them do their jobs.

ACTIVATOR

When a developing agent is dissolved in water, the solution has a neutral pH. However, the agents do *not* work well in a neutral solution - they work better in a basic (alkaline) solution. Therefore a strong base is added to the solution. This base is called an *activator* because it pushes the agents into action.

A common activator is sodium hydroxide (commonly known as lye), a strong base with a pH value of 14. Because it has such a high pH number, sodium hydroxide makes the developer work very fast. Other activators include Sodium Carbonate, Kodalk Balanced Alkali, and Borax. These other activators have progressively lower pH numbers. This means a developer containing borax will be a slower developer than the one containing sodium hydroxide.

Activators are *caustic* chemicals that can eat holes through skin. Extreme caution, including the wearing of rubber gloves, is required when working with such chemicals.

PRESERVATIVE

Another weakness of developing agents is that when exposed to oxygen they break down into their elements. This is called *oxidation* and occurs when the developer solution turns brown. To prevent oxidation, a preservative (usually *sodium sulfite*) is added to developing solutions.

RESTRAINER

A third weakness of developing agents is that they don't know when to stop. When they have finished turning exposed silver crystals black, they start to attack unexposed silver crystals. Of course, these crystals cannot be developed if the image is to be correctly produced. When some of the unexposed crystals are developed, the clear areas will no longer be clear. This darkening of the clear areas is called developmental fog or chemical fog. To prevent developmental fog or chemical fog, a restrainer (most often Potassium Bromide) is added to the developer solution.

STOP BATH

The longer the emulsion is kept in a developer, the darker the resulting image will be. When development is "just right," development must be stopped quickly. To do this, a *stop bath* is used.

A stop bath must be acidic because developers are basic. A neutral (water) can also stop development, but it takes too long and development can continue during this time. Most stop baths contain a lot of solvent (water) and a little acid, usually *acetic acid*.

Besides stopping the developing action, stop bath also helps to save the fixing bath by changing the pH of the film from basic to acid. This is necessary because fix is an acid and is an expensive solution (stop bath is inexpensive). Failure to stop the film causes the base of the developer remaining on the film to react with the acid of the fix, thus neutralizing the fix.

Acetic acid is a strong chemical and must be used carefully. Always add the acid to the water and not the water to the acid because the latter will cause considerable heat to be generated, resulting in splashes which can burn the skin.

Film Processors generally do not use stop bath. Instead, rollers squeegee off the developer from the film before it enters the fixer. In addition, fixer used in processors contain the same acetic acid to protect the fix, just in case any developer does get in.

FIX

After you have put a photographic emulsion in a stop bath, you have produced a visible image. However the image won't last long (be made permanent) until you use another solution called *fix*.

During development, exposed silver-halide crystals in the emulsion are turned into black metallic silver, but unexposed crystals are not changed. These light-sensitive crystals, when exposed to light, will start to turn into black metallic silver, thereby darkening the clear areas of the film until the film finally turns completely black. Fixer dissolves the unexposed silver halide crystals, thereby making the image permanent.

SODIUM THIOSULFATE

The first ingredient in the fixing solution is water, which is the solvent used to dissolve the other chemicals. The next ingredient is *sodium thiosulfate*, commonly called *hypo*. Sodium thiosulfate is a salt. It is the most important ingredient in the fixing solution because it dissolves the unexposed silver-halide crystals (the sodium thiosulfate is a solvent, because it dissolves the silver-halide crystals).

ACETIC ACID

Even though a solution of water and hypo will dissolve the unexposed silver-halide crystals, other chemicals are added to the fixing bath. The first of these is acetic acid, the same chemical as that used in stop bath. Its purpose is to neutralize any developer still left on the film when it enters the fix. Its purpose in the fix, then, is the same as its purpose in the stop bath.

Because film processors do not use a stop-bath solution, fix used in processors must contain more acetic acid (to protect the fix from the developer) than fix prepared for use in trays.

PRESERVER

A preservative is used both in developer and in the fixing bath. The surprising thing is that the same chemical compound, *sodium sulfite*, is usually used to preserve both solutions.

In the fixing bath, the acid added to neutralize leftover developer attacks hypo (sodium thio*sulf*ate). The hypo then breaks down into tiny pieces of *sulfur*, called *colloidal sulfur*, which hangs suspended in the fixing bath. Colloidal sulfur will not do the job hypo does. It is useless in a fixing bath. Sodium sulfite solves the problem. In an amazing chemical reaction, sodium sulfite combines with colloidal sulfur and turns it back into sodium thiosulfate. Hypo is therefore preserved by sodium thiosulfate.

HARDENER

The next ingredient in the fixer protects the gelatin in the photographic emulsion. When the emulsion is put into the developing solution, the gelatin swells up and becomes soft. This is necessary for the developer to work. Most fixing baths contain an ingredient to make the gelatin of the emulsion harden up again. A common hardener is the salt *Potassium Alum*.

If the emulsion is not hardened in the fixing bath, it may swell up and soften even more during washing. The hardener prevents excessive swelling and softening of the emulsion.

Some films *cannot* be fixed in a solution containing hardener. It is important to check with the film's manufacturer to be certain that an appropriate fix solution is used.

BUFFER

The hardener protects the photographic emulsion, but a buffer protects the hardener. It protects the hardener against an increase in pH level of the fixing bath caused by left-over developer clinging to the film when it enters the fixer. Hardeners work best when the pH of the fixing bath is at 4. The buffer, usually *Boric Acid*, keeps the level of the fixing bath at 4, thus protecting the hardener.

WASH

The last photographic processing solution is the wash. This solution normally consists of only a solvent - water.

Water is the one chemical used in all photographic processing solutions. In each one, it is used for the same purpose: to dissolve chemicals. In the wash, it dissolves and removes any chemicals left in the photographic material by the previous processing solutions, especially the fixing bath. If processing chemicals such as hypo were left on a photographic material, the image would gradually become faded and stained. Washing in water prevents this, thus making the finished film permanent.

REVIEW

The chart on the following page is a listing of the four photographic processing solutions, their component compounds and examples of chemicals used for each compound in some developers.

NAME OF PROCESSING SOLUTION	COMPONENTS	EXAMPLE CHEMICAL
DEVELOPER	Developing Agent	Hydroquinone
	Activator	Sodium Hydroxide
	Preservative	Sodium Sulfite
	Restrainer	Potassium Bromide
	Solvent	Water
STOP BATH	Neutralizer	Acetic Acid
	Solvent	Water
FIX	Silver-halide solvent	Sodium Thiosulfate
	Neutralizer	Acetic Acid
	Preserver	Sodium Sulfite
	Hardener	Potassium Alum
	Buffer	Boric Acid
	Solvent	Water
WASH	Solvent	Water

MIXING DIRECTIONS FOR KODAK DEVELOPER D-85

Use a wide-mouth container or pail for mixing the developer. First check the volume of the container and mark it to indicate the exact level of the quantity of solution to be mixed. Fill the container half full of water at about 32° C (90° F) and dissolve the chemicals in the order given. When all the chemicals have been dissolved, add cold water to the fill mark and stir thoroughly. The solution should now be transferred to clean bottles filled to the top and stoppered tightly. Allow the developer to stand for 2 hours before using. If only a portion of the contents of a bottle is used at one time, it is suggested that the balance be saved by filling a bottle of smaller size, which should then be stoppered tightly.

TIME OF DEVELOPMENT IN KODAK DEVELOPER D-85

Develop films for 1 1/2 to 2 1/4 minutes at 20° C (68° F). With a correctly timed exposure, the image should appear in 30 to 45 seconds at the temperature specified.

Kodak Developer D-85 (a lith-type developer)	**Avoirdupois**	**U.S. Liquid**	**Metric**
Water, about 30°C (90° F)	64 ounces	2 1/2 gallons	500 ml
Kodak Sodium Sulfite (Anhydrous)	4 ounces	1 1/4 pounds	30.0 grams
Paraformaldehyde	1 ounce	5 ounces	7.5 grams
Kodak Sodium Bisulfite (Anhydrous)	123 grains	1 oz, 200 grains	2.2 grams
Kodak Boric Acid, Crystals	1 ounce	5 ounces	7.5 grams
Kodak Hydroquinone	3 ounces	15 ounces	22.5 grams
Kodak Potassium Bromide (Anhydrous)	90 grains	1 ounce	1.6 grams
Water to make	1 gallon	5 gallons	1.0 liter

WHAT IS LITH PROCESSING?

WHEN TO USE LITH PROCESSING

To produce high-quality line work or to obtain a good screen dot, it is essential that the photographic system used is capable of rendering even the finest lines or smallest screen dots with optimum edge or dot sharpness and maximum density. After-treatment must also be possible, like reduction, correction, and, if necessary, making contact copies or exposure to printing plates.

This not only calls for photographic materials of intrinsic high contrast but also for developers whose composition contributes to achieve an extraordinary high density. Such developers are known as lith developers. However they are highly subject to aerial oxidation. This renders it difficult to maintain a totally stable processing quality, day in and day out, irrespective of the film processed.

After discussing the properties of lith developers, we shall further explain this unique replenishment system.

CHARACTERISTICS OF LITH DEVELOPERS:

The special property of lith developers is known as the lith effect, which consists of obtaining a very high contrast, together with favorable adjacency effects, so that lines and screen dots are perfectly delineated. This extremely high contrast is due to one of the oxidation products of the one and only developing agent, hydroquinone, used in lith developers. This oxidation product is called semiquinone. The amount of semiquinone is dependent on the quantity of sulfite. The more sulfite, the less semiquinone, and vice versa.

However, a certain sulfite content, acting as an anti-oxidant, is required to restrict the aerial oxidation of a developer. When composing a lith developer, one must search for a compromise. On the one hand, a rather large sulfite content is necessary to restrict oxidation, while on the other hand, a developer with sufficient lith effect should contain a minimum of sulfite.

For example, the addition of formol-bisulphite ensures a low level of free sulfite, without excessive aerial oxidation. Nevertheless, lith developers are always far more sensitive to aerial oxidation than other developers.

Apart from the effect of aerial oxidation on the composition of the developer, the developing agents are bound to become exhausted after the development of a certain amount of film. These two reactions alter the amounts of the various developer components in different ways.

THE PROBLEM OF COMPROMISE

Oxidation is caused by the oxygen in the air. The rate of this reaction is constant under constant processing conditions (agitation, developer temperature, ambient temperature, area of air/developer interface, and type of developer). The rate does not depend on the amount of film processed.

In the case of aerial oxidation, the following chemical changes take place:

- diminishing amount of developing agent
- high consumption of sulfite or anti-oxidant
- reduced buffering action through the formation of alkalis, causing the pH to rise
- the bromide content (restrainer) remains practically constant

The table gives some idea of the quality in the decomposition of a lith developer caused by aerial oxidation and by exhaustion through film development.

PHOTOGRAPHIC CONSEQUENCES

The two reactions, aerial oxidation and exhaustion through development, differently affect the proportions of the basic components of the developer. The two reactions, also affected by the composition of the photographic material, will, therefore, differently affect the photographic properties.

The following table shows the photographic consequences occurring in LITEX emulsions as a result of the chemical changes caused by aerial oxidation and exhaustion during development in, for example, G 90 D.

PRACTICAL CONSEQUENCES

The above shows that it is not an easy matter to compensate for the consumption of chemical components, caused by aerial oxidation and exhaustion, by means of effective replenishment systems.

Less adequate replenishment systems may cause an imbalance between the various chemical components, which, to compensate for solution decomposition caused by aerial oxidation and exhaustion, must be added in different amounts. This imbalance may produce unstable photographic results, costing time and money for remakes or necessitating additional retouching, reducing, etc.

These unprofitable and uneconomical consequences are even more marked when using sophisticated equipment like scanners, that require extremely accurate adjustment.

Since the marketing of lith developers, a number of replenishment systems have been devised, all trying to meet the dual replenishment requirements. These systems are either designed for certain types of films of individual film manufacturers, or they are one solution systems attuned to an estimated daily film throughput (Multirange, Blender), whereby in the case of deviations either a transfusion is carried out or additives are used.

These systems, therefore, require regular checking. They do not guarantee permanent stability, because of the latter, due to the compensation of deviations, can only be approximated.

	Aerial oxidation	Exhaustion
Cause of deviation	constant rate, affected by: - agitation - developer temperature - air/developer interface - type of developer	variable, dependent on: - throughput - silver content of film - image density - type of developer
Chemical changes	- less developing agent - much less antioxidant - constant bromide content - more alkali, higher pH	- less developing agent - less antioxidant - larger bromide content - less alkali, lower pH

	Aerial oxidation		Exhaustion	
	Sensitivity	**Range**	**Sensitivity**	**Range**
Developing Agent	decreases	increases slightly	decreases	increases slightly
Antioxidant	no change	decreases	increases	decreases slightly
pH	rises	drops	drops	rises slightly