CHEMISTRY FOR THE AMATEUR PHOTOGRAPHER. III. THE CHEMISTRY OF DEVELOPMENT*

When a light-sensitive material is exposed for a short time to light, although the change which takes place may be so minute that it cannot be detected by any ordinary means, if the exposed material is placed in a chemical solution, which is termed the "developer," the chlorine or bromine is taken away from the silver, and the black metallic silver which remains behind forms the image. This image is, of course, made up of grains, because the original emulsion contains the silver bromide in the form of microscopic crystals, and when the bromide is taken away from each of these, the crystal breaks up and a tiny coke-like mass of metallic silver remains behind in exactly the same position as the bromide crystal from which it was formed, so that, whereas the original emulsion consisted of microscopic crystalline grains of the sensitive silver salt, the final image consists of equally microscopic grains of black metallic silver. This removal of the bromide from the metallic silver is known chemically as reduction. (It must be remembered that chemical reduction has nothing to do with the photographic operation known as the reducing of a negative; that is, the weakening of an over-dense negative where the word simply refers to the removal of the silver and is not used in the chemical sense.)

Chemical reducers are substances which have an affinity for oxygen and which can liberate the metals from their salts, such as the charcoal which is used lo reduce iron from its ore. A developing solution is therefore one which contains a chemical reducer. All substances which are easily oxidized are, however, not developers, since in order that a reducer may be used as the photographic developer, it is necessary that it should be able to reduce exposed silver bromide but should not affect unexposed silver bromide, so that its reducing power must be within certain narrow bounds; it must be a sufficiently strong reducer to reduce the exposed silver salt, and at the same time must not affect that which has not been exposed. For practical purposes the developing agents are limited to a very few substances, almost all of which are chemically derived from benzene.

Developers

The commonest developing agents are pyrogallol (pyro), hydroquinone, monomethyl para-aminophenol sulfate (Elon), *para*-aminophenol, or para-aminophenol oxalate (Kodelon), and diaminophenol hydrochloride (Acrol).

Pyrogallol (or pyrogallic acid) is made from gallic acid, which is obtained from gall nuts imported from China. The gall nuts are fermented to obtain gallic acid, and the gallic acid is then heated in a still from which the pyrogallol is distilled over. Hydroquinone is made from benzene which is

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first converted into aniline and then oxidized. Although it is somewhat less powerful as a reducing agent than pyro, it has less propensity to give stain. It is a constituent of a majority of the better known commercial developers in use today. It keeps very well when used in tank developers because it does not oxidize as readily as pyro and is generally used in motion picture work.

Some time after pyrogallic acid and hydroquinone were in general use by photographers, there were introduced a number of new developing agents made from coal tar, which are very useful as supplements to the older developers. Several of these are based on a substance called para-aminophenol, which is made in the manufacture of dyes. When para-aminophenol is treated with methyl alcohol, the methyl part of the alcohol attaches itself to it and forms a compound called methyl-para-aminophenol, which is a more active developing agent than the para-aminophenol itself. Another developing agent of the same type is diaminophenol, which is prepared in a way similar to para-aminophenol.

Para-aminophenol, methyl-para-aminophenol and diaminophenol are all bases and the developing agents are their salts, the oxalate of para-aminophenol, the hydrochloride of diaminophenol, and the sulfate of methyl-para-aminophenol, being used.

Different reducing agents behave differently as developers. We cannot use Elon in the place of hydroquinone and get the same effect. An image developed with Elon comes up very quickly and gains density slowly, while the hydroquinone image comes up very slowly but gains density steadily and rapidly. A very little change in the temperature affects hydroquinone greatly and affects Elon very little, and in the same way a small quantity of sodium or potassium bromide affects hydroquinone and does not affect Elon nearly so much. These differences in the developing agents depend upon the chemical nature of the substances themselves, and the particular property to which these differences are due is called the "reduction potential" of the developer.

The reduction potential alone does not determine the speed with which the developer develops the image, because this depends chiefly upon the rate at which the developer diffuses into the film and on the quantity of developing agent and other substances in the developer. A high reduction potential enables a developer to continue to develop more nearly at a normal rate under adverse circumstances, such as at a low temperature or in the presence of bromide. The reduction potential of a developer, in fact, may be compared to the horse-power of an automobile which for other reasons than the power of its engine is limited in speed. If we have two automobiles and they are confined to a maximum speed of twenty miles an hour, then on level roads the one with the more powerful engine may be no faster than that with a weaker engine but in a high wind or on a more hilly road the more powerful engine will allow the automobile to keep its speed while the machine with the weaker engine will be forced to go more slowly. We could indeed, measure the horsepower of an automobile by the maximum grade which it could climb at a uniform speed of 20 miles an hour.

In development, the analogy to the hill is the addition of bromide to the developer, since the addition of bromide greatly retards development, and it is found that the higher the reduction potential of a developer, the more bromide is required to produce a given effect. If we measure the developing agents in this way, we shall find that hydroquinone has the lowest reduction potential, then pyro, then Kodelon, and finally Elon, which has the highest. Hydroquinone has so low a potential that it is rarely used alone but is generally used with Elon. Kodelon can be substituted for Elon but more Kodelon has to be used in order to produce a developer of the same strength. Developers with a high reduction potential such as Elon, and to a less extent Kodelon, make the image flash up all over at once, because they start development very quickly even in the lesser exposed portions of the emulsion, while developers of low reduction potential, like pyro and especially hydroquinone, bring up the highlights of the image first and the shadows do not fully appear until the highlights are somewhat developed.

Alkalies

Most developing agents cannot develop at all when used by themselves. With the exception of Acrol, developing agents, in order to do their work, must be in an alkaline solution, and the energy depends upon the amount of alkali present. The developers of higher reduction potentia , which bring up the image very quickly, require less alkali than those of lower reduction potential. For instance, hydroquinone is often used with caustic alkalies, while the other developing agents require only the weaker carbonated alkali.

The quantity of alkali governs the energy of a developer, and if too much alkali is present, the developer will tend to produce chemical fog while if too little alkali is present, it will be slow in its action. Alkalies also soften the gelatin of the emulsion, and consequently too alkaline a developer will produce over-swelling and will give trouble with frilling or blisters in warm weather.

The alkalies generally used for photographic work are not the caustic alkalies but the carbonates, which are salts of carbonic acid, H_2CO_3. Carbonic acid is a very weak acid, so that in solution the carbonates are not neutral but alkaline because of the predominance of the strong base over the weak acid, the carbonate being, to some extent, split up into the bicarbonate or acid carbonate and the caustic alkali. The use of a carbonate in development, therefore, represents a sort of reservoirof alkali, only a small quantity of alkali being present at any time, but more being generated by dissociation of the carbonate as it is used up. If instead of using carbonate we were to use for development a solution containing a proportional quantity of caustic alkali, we should have only a small quantity of alkali present, and it would soon be exhausted. The used carbonate, therefore, enables us to employ a small concentration of alkali and yet to keep that concentration nearly constant during use.

When a salt is dissolved in water at a high temperature until no more will dissolve and then the solution is allowed to cool, the salt will generally be deposited in crystals; sometimes, as in the case of silver nitrate, the crystals consist of the pure substance, but more often each part of the salt combines with one or more parts of water to form the crystals. This combined water is called "water of crystallization." Thus, crystals of sodium carbonate formed from a cool solution contain ten molecules of water to one of carbonate, and their composition should be written $Na_2CO_3 \cdot 10H_2O$. A molecule of sodium carbonate, Na_2CO_3, will weigh 106 units, while a molecule of water, H_2O, weighs 18 units, so that the crystals of sodium carbonate contain 106 parts by weight of sodium carbonate and 180 by weight of water, and consequently crystallized sodium carbonate contains only 37% of dry sodium carbonate. If sodium carbonate is crystallized from a hot solution, only one molecule of water is combined in the crystals with each molecule of sodium carbonate so that they have the composition $Na_2CO_3 \cdot H_2O$ and contain 85% of dry carbonate. Sodium carbonate containing ten molecules of water of crystallization loses nine of them by drying in the air and breaks up, forming the compound with one molecule of water. This last molecule of water is only removed with difficulty by heating in the air, when the dry carbonate is formed, containing only a small residual quantity of water and about 98% carbonate.

When exposed to the air chemicals often either absorb or give up water. Those which absorb water are said to be "hygroscopic," and if they absorb so much that they dissolve and form a solution they are said to be "deliquescent." Chemicals which give up water to the air, so that the crystals break down and become covered with powder, are called "efflorescent."

Sodium carbonate comes on the market in three forms: Crystals with ten molecules of water, $Na_2CO_3 \cdot 10H_2O$ containing 37% of the carbonate; crystals with one molecule of water, $Na_2CO_3 \cdot H_2O$ containing 85% of the carbonate, and the dry powder containing 98% of the carbonate. The carbonate is made by treatment of salt solution with ammonia and carbon dioxide which reacts with the salt to produce sodium bicarbonate, $NaHCO_3$. The bicarbonate is heated and half of the carbonic acid driven off, producing crude sodium carbonate, which at this stage is known as "soda ash." This is then dissolved in water, and crystals of "sal soda," containing ten molecules of water, are produced. From this a crystalline salt with either one or ten molecules of water is prepared for photographic use, but owing to the uncertainty of the composition of these crystals it is better to prepare the pure dry carbonate. This is obtained by heating the pure bicarbonate which can be precipitated from a solution of sal soda by means of carbon dioxide gas. When the bicarbonate is heated in the air, half of the carbonic acid is driven off, and sodium carbonate, Na_2CO_3, is produced according to the equation:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

The exact amount of heating is very important. If it is not done for sufficient time there will be a large quantity of bicarbonate left in the product, and bicarbonate is practically useless as an alkali in photography. On the other hand, if heating is continued too long, caustic soda will be produced. In the preparation of photographic carbonate the heating should be continued so that the material is almost pure sodium carbonate containing practically no bicarbonate. Much caustic soda would be fatal, but it is better to have a trace of caustic soda than bicarbonate.

Potassium carbonate is sometimes used instead of sodium carbonate in developer formulas. Although it is more soluble than sodium carbonate, it has the disadvantages of being more expensive and of absorbing water very readily. It must, therefore, be kept in well-sealed bottles.

Another alkali which has come into extensive use recently is borax. This chemical is recommended for use in a developer especially suited for the production of fine-grained motion picture negatives. Every photographic image is composed of tiny coke-like masses of silver bromide in the sensitive emulsion. The advantage of keeping the particles as small as possible is obvious, especially in motion picture work where the individual pictures comprising a film are enlarged several hundred times during projection. One of the causes of "graininess" or the coarsening of these tiny particles in the picture image is the fusion or clumping of the grains which occurs during development. Experiments have shown that several silver halide crystals in close proximity to each other, even though unexposed, may become developed and form a clump as a result of actual contact with an exposed crystal.

Borax or sodium tetraborate is prepared from certain calcium ores by first roasting, then boiling in sodium carbonate and bicarbonate solution, and finally crystallizing in large iron vats. A new source of borax discovered in Kern County, California in 1926 is virtually pure sodium borate and requires only dissolving, filtering, and recrystallizing to prepare it for the market. The pure salt forms large crystals readily soluble in hot water. It is used in developers for the production of fine-grained negatives and in acid hardeners for prints which are to be dried on belt driers.

Preservatives

Owing to the fact that developers are necessarily substances which have a great affinity for oxygen and that the air contains oxygen, developing solutions containing only developing agent and alkali would be rapidly spoiled from oxidation by the air. In order to make the developer keep there is added to the developing solution, in addition to the reducing agent and alkali, some sodium sulfite. Sodium sulfite has a very strong affinity for oxygen, being easily oxidized to sodium sulfate so that it protects the developer from the oxygen of the air, thus acting as a "preservative." This action of the sulfite is very easily seen with the pyrogallol developer. The oxidation product of pyrogallol is yellow, and this oxidation product which is formed in development is deposited in the film along with the silver so that if we use a pyrogallol developer without sulfite we shall get a very yellow negative, the image consisting partly of silver and partly of the oxidized pyrogallol. If we use sulfite in the developer, the image will he much less yellow because the pyrogallol will be prevented from oxidizing, the sulfite being oxidized instead, and finally if we add a great deal of sulfite, we shall get almost as blue an image as with **Elon,** the oxidation product of which is not deposited in a colored form with the silver.

Sodium sulfite is prepared by blowing sulfur dioxide gas into a solution of sodium carbonate. When sulfite is crystallized from the cooled solution it forms crystals containing seven molecules of water to one of sulfite of the composition $Na_2SO_3 \cdot 7H_2O$, which contain, when pure, 50% of dry sulfite. These crystals give up water when kept in the air and form a white powder on the surface. Since sulfite, when exposed to the air, has a tendency to oxidize to the sulfate, and as the sulfate is not a preservative, it is well to view with suspicion sulfite which has effloresced to a great extent. A quick rinse in cold water will remove the white powder from the crystals.

Sulfite free from water is produced by two methods: by drying the crystals, which produces what is called the "desiccated salt, containing about **92%** of pure sulfite, and by precipitation from hot solutions which gives a compound generally called "anhydrous" sulfite, and which contains as much as 96.5% of sulfite.

Sodium forms a number of compounds with sulfurous acid in addition to sodium sulfite itself. Thus there is sodium acid sulfite or bisulfite, $NaHSO_3$, which may be regarded as a compound of sodium sulfite with sulfurous acid:

$$\underset{\text{Sodium sulfite}}{Na_2SO_3} + \underset{\text{Sulfurous acid}}{H_2SO_3} = \underset{\text{Sodium bisulfite}}{2NaHSO_3}$$

Another, sodium metahisulfite, is a compound of sodium sulfite with sulfur dioxide:

$$\underset{\text{Sodium sulfite}}{Na_2SO_3} + \underset{\text{Sulfur dioxide}}{SO_2} = \underset{\text{Sodium metabisulfite}}{Na_2S_2O_5}$$

Since sodium bisulfite may be considered as a compound of sodium sulfite and sulfurous acid, while sodium sulfite is alkaline, bisulfite is preferable as a preservative in the case of a two-solution developer, since oxidation progresses less readily in acid than in alkaline solution.

In the case of a one-solution developer containing, say, sodium sulfite, sodium bisulfite and sodium carbonate, the bisulfite is converted to sulfite by the sodium carbonate according to the following equation:

$$NaHSO_3 + Na_2CO_3 = Na_2SO_3 + NaHCO_3$$

The sodium bisulfite neutralizes or destroys an equivalent quantity of sodium carbonate, thus reducing the proportion of alkali and therefore exerts an apparent restraining action, while the developer apparently keeps longer because some of the carbonate has been destroyed.

It might be thought from the above equation that it would be as effective and perhaps simpler to use only sodium sulfite instead of sulfite and bisulfite, but experiments have shown that the bicarbonate formed acts as an anti-fogging agent.

How to Mix Developing Solutions

A developer usually contains four ingredients as follows:

1. The *developing* agent (Elon, hydroquinone, pyro, para-aminophenol, etc.).
2. The alkali (carbonates and hydroxides of sodium, potassium, lithium and ammonium).
3. The *preservative* (sulfites, bisulfites, and meta-bisulfites of sodium and potassium).
4. The restrainer (bromides and iodides of sodium and potassium).

If a developing agent like hydroquinone is dissolved in water, the solution will either not develop at all or only very slowly, and on standing it will gradually turn brown, because of what is called oxidation or chemical combination of the hydroquinone with the oxygen present in the air in contact with the surface of the liquid. This oxidation product is of the nature of a dye and will stain fabrics or gelatin just like a dye solution.

On adding a solution of an alkali such as sodium carbonate, the hydroquinone at once becomes a developer, but at the same time the rate of oxidation is increased to such an extent that the solution very rapidly turns dark brown, and if a plate is developed in this solution it becomes stained and fogged.

If we add a little sodium bisulfite to the brown-colored solution mentioned above, the brown color or stain is bleached out and a colorless solution is obtained. Therefore, if the preservative is first added to the developer, on adding the accelerator the solution remains perfectly clear because the sulfite preserves or protects the developing agent from oxidation by the air.

As a general rule, therefore, the preservative should be dissolved first.

An exception to this rule should be observed with concentrated formulas containing the developing agent, Elon. This substance is readily soluble in warm water [about 125°F. (52°C.)] and does not oxidize rapidly. If the sulfite is dissolved before the Elon, as is the case with developers such as hydroquinone, a white precipitate often appears, especially if the sulfite solution is concentrated. This precipitate forms because Elon is a combination of an insoluble base with an acid which renders it soluble. When the acid portion is neutralized by a weak alkali such as sodium sulfite, the insoluble base is precipitated. This Elon precipitate is soluble in an excess of water and also in a sodium carbonate solution with which the base forms a soluble sodium salt. When once the Elon is dissolved, however, it takes a fairly high concentration of sulfate to bring it out of solution again, though only a low concentration of sulfite is required to prevent the Elon from dissolving. If a precipitate forms on dissolving the Elon and sulfite, this will usually redissolve on adding the carbonate and no harm has been done.

Some direction sheets recommend that a portion of the sulfite should be dissolved in order to prevent the oxidation of the Elon, then dissolve the Elon, and then the remainder of the sulfite. Many workers add a little of the solid sulfite to the Elon when dissolving the latter. This procedure is quite satisfactory, though if the Elon is dissolved alone in water at a temperature not above 125°F. (52°C.), and the sulfite dissolved immediately afterward, little or no oxidation products will be formed which would otherwise produce chemical stain.

The alkali (usually carbonate) may be added in one of three ways:

(a) Dissolve the carbonate separately and add to the cooled Elon-sulfite solution. There is danger, however, of the Elon precipitating before the carbonate is added.

(*b*) Add the solid carbonate to the Elon-sulfite solution, stirring thoroughly until dissolved.

(*c*) After dissolving the Elon, dissolve the sulfite and carbonate together, cool and add to the Elon-solution.

Bromides and iodides are added to a developer to compensate for any chemical fog produced by the developer, or inherent in the emulsion. It is immaterial at what stage the bromide is added during the mixing.

When mixing a developer the following rules should, therefore, be followed:

1. Dissolve the chemicals in the order given unless the mixing directions specify changes in the order of solution. If a formula contains both sulfite and bisulfite, it is usual to dissolve these together, that is the bisulfite is dissolved in the same order as the sulfite.

2. Dissolve each chemical completely before adding the next. If the

alkali is added before the crystals of the developing agent are dissolved, each crystal becomes oxidized at the surface and the resulting solution will give fog.

3. Mix the developer at the temperature recommended, which is usually not above 125°F. (52°C.).

4. In the case of desiccated chemicals like sodium carbonate and sodium sulfite, add the chemical to the water and not vice versa.

Two practical methods of mixing are possible, as follows:

(a) Dissolve all the chemicals in one bottle or vessel by adding the solid chemicals to the water in the correct order (in the formula the ingredients should be named in the order in which they are dissolved). For example, to mix the following formula:

	Avoirdupois	Metric
Elon	45 grains	3.1 grams
Sodium sulfite	$1^1/_2$ ozs.	45.0 grams
Hydroquinone	135 grains	9.5 grams
Sodium carbonate	$2^1/_2$ ozs.	75.0 grams
Potassium bromide	15 grains	1.1 grams
Water to make	32 ozs.	I.0 liter

proceed as follows:

Dissolve the Elon in 16 ozs. (500 cc.) of water (about 125°F.) (52°C.), then add the sulfite, and when completely dissolved, add the hydroquinone. Finally add the carbonate and bromide and cold water to make 32 ozs. (1 liter).

For large quantities the filter bag method should be used, the chemicals being placed in the bag and dissolved in the above order.

(b) An alternative method is to dissolve the preservative and developing agent in one vessel and the carbonate and bromide in another, cool and mix. This method is the safest and best for quantity production.

For example, to mix the following motion-picture developer,

	Avoirdupois	Metric
Sodium sulfite	4 lbs.	1800.0 grams
Hydroquinane	13 ozs.	390.0 grams
Sodium carbonate	4 lbs.	1800.0 grams
Potassium bromide	3 ozs.	YO.0 grams
Water to make	10 gals.	40.0 liters

proceed as follows:

Dissolve the sulfite in about one gallon (4 liters) of water (125°F.) (52°C.), then dissolve the hydroquinone and filter into the tank. Then add one gallon (4 liters) of cold water to the tank, dissolve the sodium carbonate and bromide in one gallon (4 liters) of hot water and filter this into the tank, immediately adding cold water up to ten gallons (40 liters). The object of adding cold water to the tank before adding the carbonate is to cool off the solution before the carbonate is added.

Mixing Concentrated Developers

The extent to which a developer may be concentrated is determined by the solubility of the least soluble constituent, because a stock solution should usually withstand cooling to 40°F. (4.4°C.) without any of the ingredients crystallizing out. Usually, the hydroquinone and Elon come out of solution on cooling, but this may be prevented by adding wood alcohol or methanol in a concentration up to 10%. Denatured alcohol may be used if wood alcohol has been added as the denaturant. If a precipitate forms, however, on adding the denatured alcohol to the developer, the denatured alcohol is unfit for use.

The addition of the alcohol does not prevent the other ingredients such as sodium sulfite from crystallizing out; in fact, the alcohol diminishes their solubility and therefore increases the tendency to come out of solution.

A *para*-aminophenol-carbonate developer is difficult to prepare in concentrated form, though by adding a little caustic soda the solubility of the *para*-aminophenol is increased and a stronger solution can be thus prepared.

When preparing concentrated developers it is important to observe carefully the rules of mixing, taking care to keep the temperature of the solution as low as possible if a colorless developer is to be obtained.

The following formula is a typical example of a concentrated developer and is prepared by dissolving the ingredients in the order given:

	Avoirdupois	Metric
Water (about 125°F.) (52°C.)	16 ozs.	500.00 cc.
Elon	75 grains	5.3 grams
Sodium sulfite	$2\frac{1}{2}$ ozs.	75.0 grams
Hydroquinone	$\frac{3}{4}$ oz.	22.5 grams
Sodium carbonate	$3\frac{1}{2}$ ozs.	105 0 grams
Potassium bromide	38 grains	2.7 grams
Wood alcohol	$4\frac{1}{2}$ ozs.	136.0 cc.
Cold water to make	32 ozs.	1.0 liter

Two-Solution Developers

A two-solution developer is simply a one-solution developer split into two parts, one containing the carbonate and bromide, the other containing the developing agent and preservative so that the developer will oxidize less readily and therefore keep well. The reason why it is customary to keep a developer like pyro in two solutions, is because pyro oxidizes much more readily than Elon or para-aminophenol with a given amount of preservative.

For purposes of mixing only one-solution developers need be considered because the same rules regarding mixing apply in both cases.

Using Solutions

Photographic solutions, especially developers, vary considerably in their period of usefulness or time during which they may be utilized effectively to process exposed films and papers. This "useful life," as it is sometimes called, is therefore an important property of a solution and should be studied by every one handling photographic materials. There are a good many factors which influence the useful life of a solution, such as whether it receives intermittent or continuous use, the extent of the surface exposed to the air, the temperature, the nature and reactions of the chemical constituents, and the manipulative procedure used in handling films or prints in the bath.

The Useful Life of Developers

Without Use.—If a freshly mixed developer (prepared with water boiled to free it from dissolved air) is stored in a completely filled and stoppered or wax-corked bottle, it will keep almost indefinitely even in the light. Under ordinary conditions of storage, the bottle or vessel contains more or less air. Also, when an ordinary cork or a non-airtight cover is used, the surface of the developer is continually in contact with air, the oxygen constituent of which oxidizes the developing agent and sodium sulfite present. This results in a lowering of the developing power in direct proportion to the amount of oxidation of the developing agent, which is accelerated as the preservative or sodium sulfite becomes oxidized also.

The oxidation products of developing agents are usually colored so that the developer on keeping frequently turns brown. In the presence of sodium sulfite, however, the oxidation products of hydroquinone consist of mono- and disodium sulfonates which are colorless. The fact that an old Elon-hydroquinone developer is colorless is, therefore, no indication that the original developing power is unimpaired. An oxidized Elon or Elon-hydroquinone developer also frequently fluoresces strongly.

In some cases when an Elon-hydroquinone developer gives slight developer fog when freshly mixed, the fogging tendency disappears on standing. This may be due to the anti-aerial fogging action of the developer-oxidation products which are produced on keeping.

A solution of a developing agent, such as pyro, to he stored for a considerable time, will keep best in the presence of an acid sulfite such as sodium bisulfite rather than sodium sulfite which is slightly alkaline. It is always preferable, therefore, to prepare such a developer as two solutions: one containing the developing agent and sodium bisulfite, and the other the carbonate and bromide, and to mix these solutions as required for use. A plain solution of sodium sulfite oxidizes readily in contact with air at a concentration below 10%, but above this concentration it oxidizes very slowly. Stock solutions containing sodium sulfite alone or in combination with a developing agent should be prepared, so that the concentration of the sulfite is around **10%** for maximum keeping properties. Owing to the relative insolubility of Elon in a sodium sulfite solution, it is not possible to prepare such stock solutions with Elon.

Sodium bisulfite keeps satisfactorily in more dilute solutions and is a better preservative than sulfite in the absence of carbonate. It is usual, therefore, to keep readily oxidizable developing agents such as pyro, admidol, etc., by mixing with sodium bisulfite. On adding sodium bicarbonate to sodium bisulfite, sodium sulfite and sodium bicarbonate are formed, so that in compounding a two-solution formula from a one-solution formula it is necessary to take care of this neutralization of the carbonate by using an extra quantity.

Single solution developers containing sodium hydroxide or potassium hydroxide do not keep unless well stoppered, pure gum rubber stoppers being most suitable.

With Use.—During development, several reactions are taking place: **(1)** The developing agent and sulfite are being oxidized by the air; (2) the developing agent is being destroyed as a result of performing useful work in reducing the exposed silver halide emulsion to metallic silver; and **(3)** oxidation products of the developer and the by-products, sodium hromide and sodium iodide, are accumulating. The hromide and iodide and developer oxidation products restrain development while the oxidation products prevent aerial fog. The restraining action of the bromide and iodide is analogous to cutting down the exposure, so that with an old developer it is not possible even on prolonged development to get the ultimate result out of an under-exposure.

The time required to produce a definite contrast increases as a developer is used, and the solution ceases to be useful when the time required for this exceeds the maximum time which can be allotted for the developing operation. **A** deep tank developer, for example, is therefore discarded for one or more of the following reasons: **(1)** the time for complete development is excessively long; *(2)* the solution stains or fogs emulsions badly; and **(3)** the accumulation of by-products is so great that shadow detail is lost even with full development.

Developer Troubles

The Developer Gives Fog.—Fog is the chief trouble caused by faulty mixing. It may be a result of violation of the rules of mixing such as dissolving the carbonate before the sulfite, mixing the solution too hot, omitting the bromide, adding too much carbonate or too little sulfite, the use of impure chemicals, etc.

With certain developers, notably those containing Elon and hydroquinone, a form of fog, known as aerial fog, is produced when film wet with developing solution is exposed to the air. Motion picture positive film developed on a reel is especially sensitive to aerial fog. It may be prevented by adding about 5% of old developer to the freshly mixed developer. This is more effective than increasing the concentration of bromide above the normal quantity added. The oxidized developer probably acts as an anti-fogging agent thus reducing the tendency for fog formation.

Negatives developed in a developer containing an excess of sulfite or one containing hypo or ammonia may show *dichroic* or *green fog*. This appears yellowish green by reflected light, and a pink color by transmitted light. It is usually caused when the dissolved silver salts, under certain conditions, are reduced to metallic silver in a very fine state of subdivision, particularly in the shadow portions of the negative where no bromide is liberated during development. Fine-grained emulsions are most susceptible to this form of fog.

Some deep tank developers may begin to fog a short time after they have been put into use. When this occurs it usually can be traced to the presence of sulfide in the solution caused by the action of bacteria which reduced the sulfite in the developer to sulfide. The fog may be cleared up by putting some waste film or plates through the solution or by adding a small quantity of lead acetate to the developer. The bacteria or fungi usually grow in the slimy deposit which accumulates on the inner walls of the tank. This deposit may be removed by sterilizing the container occasionally with bleaching powder.

The Solution is Colored.—As a general rule, the developer when mixed should be colorless and if colored it should be suspected as being likely to give fog. In the case of a pyro developer mixed with bisulfite, which contains iron, an inky substance is formed as a combination product of the iron and the pyro, and this imparts a dirty bluish red color to the solution, although photographically it is harmless. If a two-solution pyro developer is mixed in dirty vessels the B solution (which contains the carbonate and bromide) may be colored brown by the presence of a little pyro.

The Solution Does Not Develop.—Omission of the developing agent or the carbonate may usually be suspected if a developer does not develop.

Precipitation of a White Sludge.—If a white precipitate settles on standing, this is probably Elon. The precipitate may often be redissolved by adding 5% of wood alcohol or methanol, but if this is not successful, then the formula contains either too much Elon or sulfite or not enough carbonate. If it is known that the formula gives a clear solution when mixed correctly and should the Elon precipitate out during mixing when the sulfite is added, the precipitate will usually redissolve on adding the carbonate. If the final solution is not colored, no harm will have been done.

Scum.—Scum may be picked up on films or plates from the surface of the developer especially if the solution has been allowed to stand unused for several days. The scum may consist of grease, solid matter, or developer oxidation products, especially if the developer contains pyro. The scum should be removed by passing the edge of a blotting paper along the surface of the solution or by using a skimmer, consisting of several layers of cheese cloth stretched over a square wire frame.

Miscellaneous Troubles.—Various types of developer stains may be produced on films, plates, and papers. When a developer solution is not agitated sufficiently during the progress of development, characteristic markings are produced. This is occasionally observed with film developed on hangers or racks. These markings are usually the result of retardation of development along the sides of a hangar or rack caused by the accumulation of oxidized developer products and sodium bromide. They may he prevented by thorough agitation of the holder or rack during development.

The Importance of Rinsing

It is important to rinse films, plates, and papers after development and before fixation. When a film or print is transferred from the developer directly to the fixing bath the alkali in the developer retained by the film or print neutralizes some of the acid of the fixing bath. The addition of developer also gradually destroys the hardening properties of the fixing bath. Therefore, by removing as much developer as possible from the film or print by thoroughly rinsing in water or an acid rinse bath for 10 or 20 seconds, the life of the fixing bath is very much prolonged, while the tendency for stains and blisters to form is very much reduced.

Study Methods of Testing Radioactivity of Water. With a market flooded with waters, salves, hair tonics, tissue creams, mouth washes, healing pads and other preparations alleged to have great healing power because of their radioactivity, government chemists are working on suitable means of detecting the presence or absence of radioactive substances in water and drugs.

At the recent meeting in Washington of the Association of Official Agricultural Chemists, J. W. Sale of the U. S. Department of Agriculture, reported on one method of testing radioactivity. He recommended further checking of the method by chemists, before official adoption by the association.

The discovery of the curative properties of radioactive substances has resulted, among other things, in the production of solid, semi-solid and liquid preparations which are beina sold as possessing sufficient radioactivity to cure all kinds of conditions. A recent government survey of such waters and drugs revealed that their medicinal efficacy was much misrepresented. Action will he taken under the Federal Food and Drugs Act against shipments of the alleged radioactive products which are falsely or fraudulently misbranded under the terms of the law.

Radium and radioactive substances have possibilities of great harm as well as great good, it is declared. Using them indiscriminately without adequate supervision is extremely dangerous.—Science Service