CHEMISTRY FOR THE AMATEUR PHOTOGRAPHER. I. THE CHEMISTRY OF PHOTOGRAPHIC MATERIALS*

The art of photography is founded upon the fact that the compounds of silver, and especially its compounds with chlorine, bromine, and iodine, are sensitive to light.

The earliest photographs were made by coating paper with silver chloride and using this to form images by its darkening under the action of light, but the sensitiveness of the silver chloride was too slight to use it in this way to form images in the camera.

To get results which require less exposure to light, advantage is taken of the fact that it is not necessary for the light to do the whole work of forming the image; it is possible to expose the silver salt for only a short time to the light and then to continue the production of the image by chemical action, the process being termed "development."

Sensitive photographic materials therefore consist of paper, film, or glass, coated with a layer in which is suspended the sensitive silver bromide or silver chloride. This layer is called the *emulsion*. The emulsion consists of a suspension of the silver salt in a solution of gelatin. If there were no gelatin in the solution the silver compound would settle to the bottom and an emulsion would not be formed, but the gelatin prevents the settling so that the precipitated silver salt is uniformly distributed through the solution.

Photographic materials which are to be developed must contain no excess of soluble silver and the emulsion must be made so that there is always an excess of bromide or chloride, since any excess of soluble silver will produce a heavy fog over the whole of the surface as soon as the material is placed in the developer. In the case of Solio paper, however, which is not used for development but which is printed out, a chloride emulsion is made with an excess of silver nitrate. This causes rapid darkening in the light so that prints made upon Solio paper are not developed, the visible image being toned and fixed. Solio paper can be developed with certain precautions, such as by the use of acid developers or after treatment with bromide to remove the excess of silver nitrate.

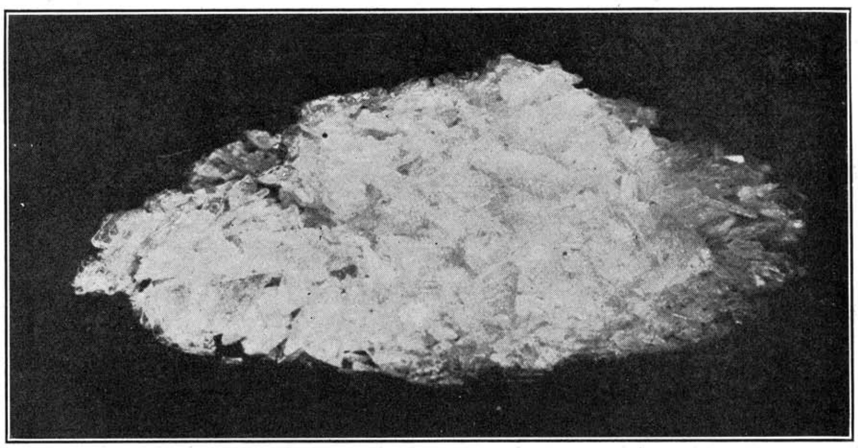
In the early days of photography prints were usually made on printing-out papers, but at the present time most prints are made by the use of developing-out chloride and bromide papers, which are chemically of the same nature as the negative-making materials and are coated with emulsions containing no free silver nitrate.

* This series of articles is based upon selected chapters from "Elementary Photographic Chemistry" and "The Fundamentals of Photography," by Dr. C. E. K. Mees, published by the Eastman Kodak Company, Rochester, New York. Cuts also are by courtesy of the Eastman Kodak Co.

Negative-making materials such as plates and films always contain silver bromide with a small addition of silver iodide. The different degrees of sensitiveness are obtained by varying the temperature and the duration of heating which the emulsions undergo during manufacture, the most sensitive emulsions being heated to higher temperatures and for a longer time than the slower emulsions.

If a slow bromide emulsion is coated upon paper, the material is known as *bromide paper* and is used for printing, and especially for making enlargements. The less sensitive papers which are commonly used for contact printing by artificial light contain silver chloride in the place of silver bromide.

In order to obtain silver nitrate the first step is to dissolve metallic silver in nitric acid. The silver replaces the hydrogen of the acid and forms



CRYSTALS OF SILVER NITRATE

silver nitrate, the hydrogen liberated decomposing a further portion of the nitric acid. The silver nitrate is crystallized out of the solution and obtained in colorless, transparent plates.

Silver nitrate for photographic use has to be extremely pure, and since metallic silver usually contains a small quantity of other metals, such as copper and lead, it is necessary to free it from these impurities. This is accomplished by recrystallization, so that the silver nitrate is finally obtained in a perfectly pure form.

Silver nitrate is very soluble in water. It attacks organic material, and blackens skin, wood, cloth, and other similar substances on exposure to light.

When a solution of silver nitrate is added to a solution of a bromide or chloride of another element, a reaction occurs and the insoluble silver bromide or chloride is precipitated. Thus, if we add silver nitrate to potassium bromide, the reaction occurs according to the following equation:

$$AgNO_3 + KBr \longrightarrow AgBr + KNO_3$$

The potassium nitrate formed remains in solution, but if the solution is at all concentrated, the silver bromide is thrown down as a thick, curdy precipitate.

The bromides and chlorides used in photography are chiefly the salts of potassium and sodium. Both the bromides and the chlorides are obtained from naturally occurring salt deposits, but, whereas these deposits consist chiefly of chlorides, they contain only a very small quantity of bromide, and bromide is therefore a very much more expensive material than chloride.

The elements chlorine, bromine, and iodine are all obtained from natural salt or from the sea, iodine being derived from certain sea weeds which extract it from the sea water and thus make it available in a concentrated form. Chlorine is a yellowish green gas, very suffocating and poisonous, bromine gives dark red fumes which are even more noxious than chlorine and condense to a liquid, and iodine forms shining, black crystalline flakes which on heating give a violet vapor. The chief chlorides, bromides, and iodides used in photography are the following:

Ammonium Chloride: White crystals soluble in water. Made from ammonia and hydrochloric acid, should have no odor, and when evaporated by heat should leave no residue behind.

Ammonium Bromide: Very similar to the chloride, which is the only impurity likely to be present.

Ammonium Iodide: Should consist of colorless crystals. Decomposes in light and is stained yellow by the iodine liberated. Very soluble in water and deliquescent. Soluble in alcohol.

Sodium Chloride: Ordinary table salt is fairly pure sodium chloride and a very pure salt is easily obtained. The pure salt is stable and not deliquescent. Soluble in cold water (40°F.) (4°C.) to the extent of 31 ounces of salt to 100 fluid ounces of solution. Solubility increases very little on heating.

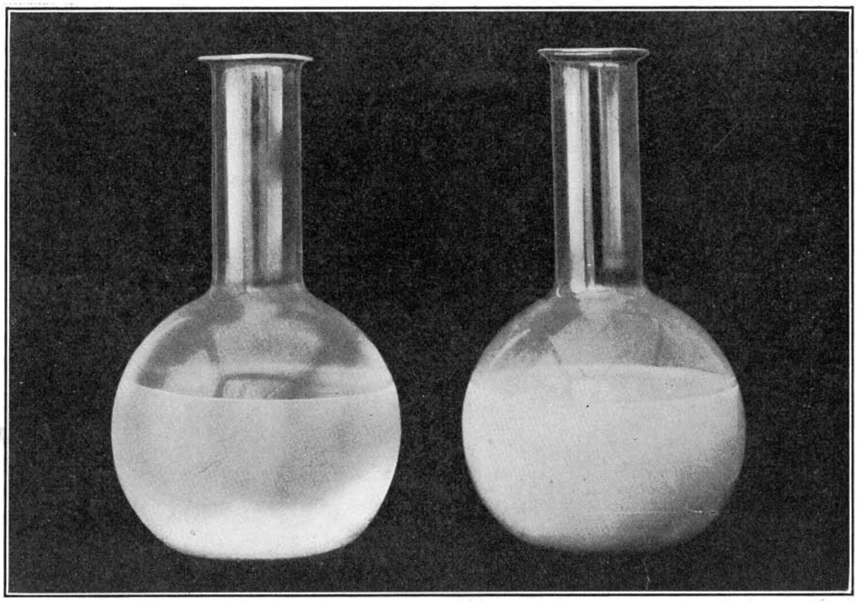
Sodium Bromide: A white salt, similar to the chloride but more soluble. Is generally pure but may contain chloride.

Potassium Chloride: White salt, very similar to sodium chloride.

Potassium Bromide: Occurs as colorless cubical crystals and is generally pure. To facilitate handling and weighing, potassium bromide is usually supplied in the granular form. Very soluble in water.

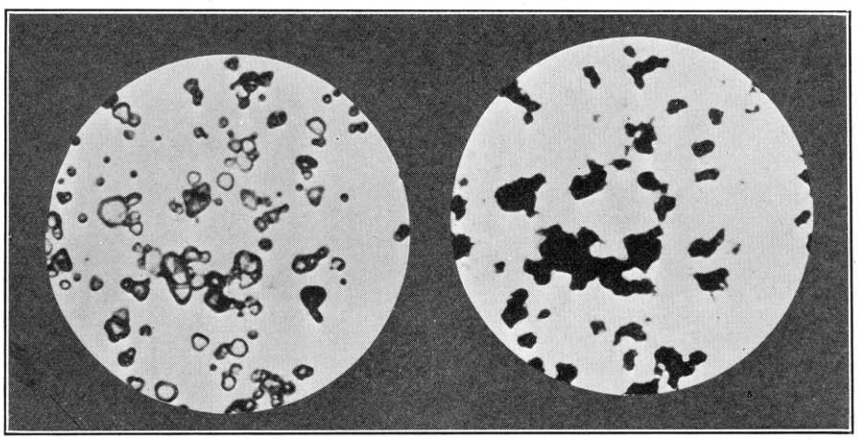
Potassium Iodide: Similar to bromide. Very soluble. May contain as impurities carbonate, sulfate, and iodate, but is usually pure. A solution of potassium iodide dissolves iodine, which is insoluble in water, and it is therefore used to prepare a solution of iodine.

The gelatin which is used to emulsify the sensitive silver salts is a very complex substance which is obtained from the bones and skins of animals.



TWO FLASKS CONTAINING PRECIPITATED SILVER BROMIDE

The flask on the left shows that silver bromide without gelatin settles to the bottom of the solution. The one on the right shows the silver bromide held evenly in suspension by gelatin.



CRYSTALS OF SILVER BROMIDE BEFORE (LEFT) AND AFTER (RIGHT) DEVELOPMENT

The photographs above, taken through a very powerful microscope, show crystals of silver bromide before development (on the left) and (on the right) some crystals after they have been changed into metallic silver by development. The crystals before development are transparent except where they are seen sideways or where their edges appear darker. After development the clear yellow silver bromide is turned into a black coke-like mass of silver in exactly the same position as the crystal from which it was formed.

Gelatin has some curious and valuable properties. In cold water it does not dissolve but it swells as if, instead of the gelatin dissolving in the water, the water dissolves in the gelatin. If the water is heated, the gelatin will dissolve, and it can be dissolved to any extent. It cannot be said that there is a definite solubility of gelatin in water in the same sense as salts may be considered to have a definite solubility. As more gelatin is added, the solution becomes thicker. If the gelatin solution is heated, it will become thinner and less viscous when hot, and will thicken again as it cools, but it will remain thinner than if it had not been heated so that the heating of the gelatin solution produces a permanent change in its properties. If a gelatin solution is cooled, the gelatin will not separate from the solution in a dry state but the whole solution will set to a jelly. If the jelly is heated again, it will melt, and a jelly can be melted and reset many times. During the treatment there will be produced a progressive change in the jelly, and if the process is continued long enough, the solution will refuse to set and will remain as a thick liquid.

In the preparation of a photographic emulsion the gelatin is soaked in water, and then when it is swollen it is dissolved by putting it in warm water and gently warming and shaking until it is all dissolved. Then there is added to this the right quantity of bromide. The bromide dissolves in the gelatin solution just as salt would, and is stirred up to get it evenly distributed. Meanwhile, some silver nitrate has been weighed out so that the right amount is taken to act with the amount of bromide chosen and is dissolved in water, in which it dissolves very easily. This silver nitrate solution is then added slowly to the bromide dissolved in the gelatin, and produces at once a precipitate of silver bromide. The silver bromide is sensitive to light so that before adding the silver nitrate to the bromide and gelatin all the white lights are turned out and the silver is added by the light of a photographic red lamp.

As the silver is added a little at a time, the solution being stirred meanwhile, the gelatin becomes full of the smoothly, evenly precipitated silver bromide distributed through the solution.

If the emulsion of silver bromide in gelatin is coated on the film and then cooled, the gelatin will set to a jelly, still containing the silver bromide suspended in it, and then when this layer is dried, we get the smooth yellowish coating, which is familiar to those of us who have looked at an undeveloped film in the light.

If we look at the silver bromide film through a very high power microscope, we shall find that the silver bromide is distributed throughout it in the form of tiny crystals. These crystals are in the form of flat triangular or hexagonal plates, and careful investigation has shown that they belong to the regular system of crystals. When these crystals are exposed to light, no visible change takes place, but there must be some change because when a crystal of silver bromide, which has been exposed to light, is put into a developer, the developer takes the bromine away from the silver and leaves instead of the crystal what looks under a microscope like a tiny mass of coke, which is, really, the metallic silver itself freed from the presence of the bromine.

It may seem strange that silver, which we always think of as a bright, shiny metal should look black, but when it is divided up in this irregular way, it looks black, although it is the same thing as the shiny metal we are familiar with, just as a black lump of coke is the same thing as the bright gleaming diamond. If the silver bromide has not been exposed to light, then the developer has no power to take away the bromine from the silver.

Wherever, then, the light in the camera has acted upon the silver bromide crystals in the emulsion, the developer turns them into black grains of silver and we get an image, and where the light has not acted the developer has no action and no image is produced. The chemical part played by a developer, therefore, is the freeing of the metallic silver from the bromine associated with it.

Gelatin belongs to the class of substances which are called colloids, the name being derived from a Greek word meaning "gummy." When a gelatin jelly is dried it shrinks and forms a horny or glassy layer of the gelatin itself, smooth and rather brittle. This dry gelatin, when placed in water, will at once absorb the water and swell up again to form a jelly. This swelling and shrinking are of great importance in photography. When a photographic material with an emulsion made with gelatin is placed in water, the film will swell up and will continue to absorb more water and swell for a long time, finally becoming soft and even dissolving, the extent to which this occurs depending on the temperature and the nature of the solutions in which it is placed. A small quantity of either an acid or alkali will produce a considerable increase in the swelling, and since the developer is alkaline and the fixing bath is acid, both these solutions have a great tendency to swell the gelatin, especially when they are warm. In order to avoid difficulty from this source, gelatin emulsions have a hardener added before they are coated, gelatin being hardened and made more resistant to swelling by the addition of alum.

Under ordinary circumstances no difficulty is experienced by the photographer due to the softening of the gelatin, but when photographic materials are exposed to extreme temperatures, care must be taken in handling them. Hardening agents, such as alum, must be added to the fixing bath, and all solutions must be kept at the same temperature in order to avoid sudden contractions or expansions of the gelatin which may result in detaching the film from its support or in the production of reticulation, *i. e.*, a coarse wrinkling all over the film.