CHEMISTRY FOR THE AMATEUR PHOTOGRAPHER. V. REDUCTION, INTENSIFICATION, AND TONING*

Reduction

By reduction in photography is meant the removal of some silver from the image so as to produce a less intense image. Thus, in the case of an over-developed film or plate there will be too much density and contrast, and the negative may be reduced to lessen this. In the case of an over-exposed negative there may not be an excess of contrast but the negative will be too dense all over, and in this case what is required is the removal of the excess density.

It is unfortunate that the word "reduction" is used in English for this process. In other languages the word "weakening" is used, and this is undoubtedly a better word, because the chemical action involved in the removal of silver from a negative is oxidation, and the use of the word reduction leads to confusion with true chemical reduction, such as occurs in development.

All the photographic reducers are oxidizing agents, and almost any strong oxidizing agent will act as a photographic reducer and will remove silver, but various oxidizing agents behave differently in respect to the high lights and shadows of the image. Reducing solutions can be classified in three classes:

A. Cutting reducers
B. True scale reducers
C. Flattening reducers.

A. The cutting reducers remove an equal quantity of silver from all parts of the image, and consequently remove a larger proportion of the image from the shadows than from the high lights of the negative. The typical cutting reducer is that known as *Farmer's Reducer*, consisting of a mixture of potassium ferricyanide and hypo, the potassium ferricyanide oxidizing the silver to silver ferrocyanide and the hypo dissolving the latter compound. Farmer's Reducer will not keep when mixed, decomposing rapidly, so that it is usually prepared by making a strong solution of the ferricyanide and then adding a few drops of this to a hypo solution when the reducer is required. It is especially useful for cleaning negatives or lantern slides which show slight fog, and is also used for local reduction, the solution being applied with a brush or a wad of absorbent cotton.

FARMER'S REDUCER

Solution A

	Avoirdupois	Metric
Potassium Ferricyanide	15 grains	1.0 gram
Water	1 ounce	32.0 cc.

* 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.

Solution B

Hypo	1 ounce	30.0 grams
Water	32 ounces	1.0 liter

Another cutting reducer is permanganate. The permanganates are very strong oxidizing agents, and if a solution of permanganate containing sulfuric acid is applied to a negative, it will oxidize the silver to silver sulfate, which is sufficiently soluble in water to be dissolved.

PERMANGANATE REDUCER

Stock Solution A

	Avoirdupois	Metric
Water	32 ounces	1.0 liter
Potassium Permanganate	$1^3/_4$ ounces	52.5 grams

Stock Solution B

Cold water	32 ounces	1.0 liter
Sulfuric Acid C. P.	1 ounce	32.0 cc.

Permanganate has only a very weak action on a negative if no acid is present and this may be made use of for the removal of "dichroic" fog, the yellow or pink stain sometimes produced in development. Dichroic fog consists of very finely divided silver and this is attacked by a solution of plain permanganate (about 0.25%) which will have no appreciable action on the silver of the image.

An important difference should be noted between the behavior of ferricyanide and permanganate when used for reducing pyro-developed negatives. In a negative developed with pyro the image consists partly of the oxidation product of the pyro associated with the silver. When such a negative is reduced with ferricyanide the silver is removed but the stain is unattacked so that the negative appears to become yellower during reduction, though the ferricyanide does not really produce the color, only making it evident by removal of the silver. Permanganate, on the other hand, attacks the stain image in preference to the silver and consequently makes the negative less yellow. Permanganate can also be used as an alternative to ferricyanide for bleaching negatives, since if bromide be added to the solution, silver bromide will be formed and the same bleaching action obtained as with ferricyanide.

In addition to its use for reduction and bleaching, permanganate is employed as a test for hypo, since it is at once reduced by hypo, and the colored solution of the permanganate, therefore, loses its color in the presence of any hypo. It may consequently be used to test the thoroughness of the elimination of hypo from negatives or prints in washing. When permanganate is reduced in the absence of an excess of free acid, a brownish precipitate of manganese dioxide is obtained and sometimes negatives or prints which have been treated with permanganate are stained brown by

this material. Fortunately, manganese dioxide is removed by bisulfite, which reduces it still further, forming a soluble manganese salt. The brown stain can, therefore, be removed by immersion of the stained material in a solution of bisulfite.

A very powerful cutting reducer is made from a solution of iodine in potassium iodide, to which potassium cyanide has been added to dissolve the silver iodide formed during reduction. Iodine is not soluble in water but is soluble in a solution of potassium iodide. To make up the reducer a few iodine crystals are dissolved in a 10% solution of potassium iodide, and five parts of this are added to one part of a 10% solution of potassium cyanide, making up to 100 parts with water for use.

B. Proportional reducers are those which act on all parts of the negative in proportion to the quantity of silver present there; hence they exactly undo the action of development, since during development the density of all parts of the negative increases proportionally. A correctly exposed but over-developed negative should be reduced with a proportional reducer. Unfortunately, there are no single substances which form exactly proportional reducers, but by mixing permanganate, which is a slightly cutting reducer, with persulfate, which is a flattening reducer, a proportional reducer may be obtained.

PROPORTIONAL REDUCER

Stock Solution A

	Avoirdupois	Metric
Water	32 ounces	1.0 liter
Potassium Permanganate	4 grains	0.3 gram
Sulfuric Acid (10% solution)	1/2 ounce	16.0 cc.

Stock Solution B

Water	96 ounces	3.0 liters
Ammonium Persulfate	3 ounces	90.0 grams

C. Flattening reducers are those which act very much more on the heavy deposits than on the light deposits of the negative, and which will consequently reduce the high lights without affecting the detail in the shadows. Only one such reducer is known, and this is ammonium persulfate. Ammonium persulfate is a powerful oxidizing agent and attacks the silver of the negative, transforming it into silver sulfate, which dissolves in the solution. It must be used in an acid solution and is somewhat uncertain in its behavior, occasionally refusing to act, and always acting more rapidly as the reduction progresses.

Ammonium persulfate is a white crystalline salt, stable when dry. It has been found in the Research Laboratories of the Eastman Kodak Company that the action of persulfate depends largely upon its containing a very small quantity of iron salt as an impurity, and that its capricious

behavior is due to variations in the quantity of iron present. The persulfate supplied as an Eastman Tested Chemical may be relied upon to give a uniform action in reduction.

PERSULFATE REDUCER

Stock Solution

	Avoirdupois	Metric
Water	32 ounces	1.0 liter
Ammonium Persulfate	2 ounces	60.0 grams
Sulfuric Acid C. P.	3/4 dram	3.0 cc.

Intensification

Intensification is photographically the opposite of reduction, the object being to increase contrast. This is done by the deposition of some material on the silver image. A silver image, for instance, can be very much intensified by toning it with uranium, the reddish brown uranium ferrocyanide having very great printing strength and converting a weak negative into one having a great effective contrast for printing purposes. Usually, however, intensification is performed by depositing a silver, mercury, or a chromium compound upon the image, and many photographic intensifiers depend upon the use of mercury. But experience has shown that mercury-intensified images are not as stable as images produced by chromium intensification.

Mercury is a metal which forms two series of salts, the mercuric salts, which are in a higher degree of oxidation, and the mercurous salts.

Many of the mercuric salts are insoluble in water, but mercuric chloride is sufficiently soluble for practical use, and when a silver image is placed in a solution of mercuric chloride, this reacts with the silver and forms a mixture of mercurous chloride and silver chloride.

The bleached image, which appears white, can then be treated in various ways. If it is developed, for instance, both the silver chloride and the mercurous chloride will be reduced to the metal, and in addition to the silver, with which we started, we shall have added to every part of silver an equal part of mercury. Instead of using a developer we may blacken the image with ammonia, which forms a black mercury ammonium chloride and produces a high degree of intensification.

A very powerful method of intensification, used chiefly for negatives made by photo-engravers, is obtained by leaching with mercuric chloride and blackening with silver dissolved in potassium cyanide. The use of the cyanide cuts the shadows very slightly at the same time that the high lights are intensified, so that a great increase in the contrast of the negative is obtained. This is usually known as the *"Monckhoven" Intensifier.*

In the case of the chromium intensifier the silver image is bleached with

a solution of bichromate containing a very little hydrochloric acid, bichromate being an oxidizer of the same type as permanganate or ferricyanide. The image is then redeveloped and will be found to be intensified to an appreciable extent. This intensifier has found increasing favor owing to the ease and certainty of its operation and the permanency of the intensified image.

A CO-ED STUDIES CHEMISTRY

Well, my dear, I went to my first chemistry class today and I simply adore it. The instructor asked Mabel what "Chemistry" meant and she told him that she thought it meant the art of designing chemises, then he asked me the formula for alcohol and I simply had to admit that I didn't know but I told him I had a perfectly delicious gin formula if he wanted that. He said no, that gin was not included in the course, and then asked me to name some of the elements, so I named thunder, lightning, storms, and the like and he wanted to know what kind of elements those were. I told him those were the elements when they were let loose. He showed us some of the cutest tricks with little gadgets which he had on the table. He said now here is some hydro-something acid which I am going to mix with lime-water, and it foamed up all over the place. He asked Ethel what it was, then Sue whispered over and said "Seidlitz," but Ethel said it might be a Martini for all she knew. Then he filled a little doojigger with water and said now when I throw this mineral in it you will see a perfect example of chemical combination. When he did, my dear, the whole thing exploded with the most adorable noise, and simply filled the whole room with smoke. He said that would be about enough for today and that he would take us in the lavatory tomorrow where they keep the elements. Isn't it perfectly thrilling?

HENRY DUNBAR in *College Life*

Eijkman, Hopkins Share Nobel Prize in Medicine. Two men who gave to the world the earliest knowledge of the all-important vitamins, Prof. Christian Eijkman, of the University of Utrecht in Holland, and Sir Frederick Gowland Hopkins, professor of biochemistry at the University of Cambridge, England, have been awarded the 1929 Nobel Prize in medicine.

Prof. Eijkman was the first man to produce experimentally a disease of dietary origin. In 1889, when director of the hygienic laboratory at Batavia, Dutch East Indies, he succeeded in producing polyneuritis in fowl by feeding them a diet consisting exclusively of completely polished rice. He had previously noted that this disease resembled closely the disease beriberi occurring in human beings. In both the human and fowl disease, the nerves show the same degeneration, and the symptoms are very similar. In 1921 Professor Eijkman was made a foreign associate member of the National Academy of Sciences in Washington.

Professor Hopkins, in 1906, first demonstrated that an accessory food substance besides proteins, fats, and carbohydrates was necessary for growth, reproduction, and maintenance of life in animals. Since then he has done considerable research on the nature of these accessory substances, which we know by the name of vitamins. Professor Hopkins has been called discoverer of the vitamins.

These two scientists were awarded the Nobel Prize for their researches on the vitamins.—*Science Service*