

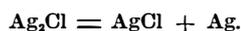
Toning Photographic Prints*

Methods Used to Bring Out the Shades and Shadows in Various Colors

THE toning operation has for its purpose the development of the shades and shadows in the ordinary photographic print by subjecting it to the action of various chemicals which produce different color effects in the picture. For this purpose, photographic papers are divided into two classes. The first class, called "direct printing papers" consist of those papers such as "silver citrate paper," "albuminous paper," "ordinary blueprint paper," "celluloidine paper," "cello," etc., which print directly on exposure to light so that it is possible to watch the formation of the picture and stop it at any desired point. The second class of photographic paper must be developed after exposure before the picture appears. Such papers are "gelatin bromide, gelatin chloride, gelatin chlorobromide paper."

DIRECT PRINTING PAPERS

The active constituent of these papers consists of an emulsion of silver chloride in gelatin, albumen or colloidon in the presence of citric acid and an excess of a soluble silver salt (citrate or nitrate). The latter absorbs the chlorine, disengaged in the decomposition of the silver chloride by exposure to light. The soluble silver salts are removed by washing and the undecomposed chloride of silver by means of a "hypo" bath. At the same time the subchloride of silver (Ag_2Cl), which forms the image, is converted into the chloride of silver and the metal itself:



The picture produced is brownish purple in color at first, changing into a reddish yellow tone after fixation. The toning operation improves the color of the picture, and, what is more, lends permanency to it.

TONING OF DIRECT PRINTING PAPERS

This is accomplished entirely by the aid of gold and platinum salts, and also the salts of the platinum group of metals. The colors that are obtained lie between black and brown, in reddish, bluish or purplish shades. Toning can be effected before or after fixing.

GOLD TONING

Either auric chloride (AuCl_3) or protochloride of gold (AuCl) can be used for this purpose, preferably the latter, for then the clearness of the picture is not impaired by the substitution of too much of the gold for the original silver. The reactions, taking place, are as follows:



The color of the picture varies from an orange red to a violet black, according to the quantity of gold that replaces the silver. The degree of the alkalinity or the acidity of the toning bath affects the tints in the picture as well. One point that must be observed carefully is that the excess of the soluble silver salt (silver nitrate or silver citrate) must be washed out before the toning operation, as otherwise the gold chloride is decomposed and a part of the gold is rendered useless for toning.

PREPARATION OF THE TONING BATHS

The bath is made by adding a weak alkaline reagent such as bicarbonate of soda, acetate of soda, borax, magnesia, carbonate of lime, etc., to a solution of auric chloride until the yellow color of the same has disappeared, indicating the transformation of the salt into the protochloride of gold (AuCl)

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which is colorless. It is very important that the toning bath be either neutral or what is better slightly acid. If the bath is alkaline the excess of the alkali decomposes the active principal AuCl to form suboxide of gold (Au_2O). This black powder then discolors in the alkali to form a subaurite of gold, which is colorless but without any action in toning. The more alkaline the bath, the more rapidly it loses its potency. For this reason the use of sodium acetate is preferred in that it leaves the bath slightly acid. The insoluble basic compounds such as CaCO_3 , give neutral toning baths, which keep their effectiveness much longer than the alkaline baths and are just as potent.

TONING AND FIXING COMBINED

It is possible to accomplish both the operations of toning and fixing in one bath. The bath must contain (1) chloride of gold and (2) sodium thiosulphate (hypo). The function of the latter is not only to dissolve the AgCl but to form a hyposulphite of gold and sodium with AuCl_3 , which then forms the active principle of the toning bath.

Various other substances may be added to the bath as follows:

- Alum, to tan the gelatin. [Formalin is preferable to alum for this purpose, as alum reacts with $\text{Na}_2\text{S}_2\text{O}_3$ (hypo)]
- Acetate of soda, to avoid the precipitation of sulphur as a result of the above reaction.
- Lead salts (acetate or nitrate) to increase the potency of the toning bath.

The action of the lead salts is very much like that of a catalyst, as a very small quantity will promote the deposition of a large amount of gold. It is known that the reactions that take place are very complex and that a large variety of compounds are formed. It appears that the lead first replaces a part of the silver in the picture, which is then replaced more readily by gold.

The lack of permanency in photographs subjected to the combined action of a toning-fixing bath has been known for some time. This has been found to be due to the hypo left behind on the print. Careful washing will eliminate all traces of the salt and give pictures which are lasting.

TONING IN PLATINUM

Photographs may be toned in platinum directly from the silver image or else from the gold toned image. Blacker shades are obtained than with gold. The platinum salt used for this purpose is potassium chloroplatinate and the reaction that ensues is as follows:



It is essential that the bath be acid. It is preferable to acidify by means of the mineral acids, such as sulphuric and phosphoric, as the organic acids are reduced with precipitation of platinum. The combined toning-fixing bath cannot be used for the reason that the acid in the solution would decompose the hypo. Salts of other metals in the platinum group, such as palladium, iridium and osmium, act in a similar manner. The chloropalladate of potassium has been used as a substitute for platinum for economical reasons. Nitric acid, being a strong oxidizing agent, cannot be used in platinum toning.

Gold-toning baths become inactive when the Au content is reduced to 30 per cent. Platinum baths can be exhausted to a far greater degree before becoming impotent, the platinum content being 11 per cent at that point. Silver pictures toned

with platinum still contain about 25 to 30 per cent of the original silver. In gold toning the silver content is very much higher.

MODIFYING THE COLOR BY PHYSICAL DEVELOPMENT

A wide range of color tones can be obtained by subjecting photographs on print paper which has been exposed only slightly to light to the action of physical developers. Much finer results are obtained than in the toning process. The distinction between physical and chemical developers lies in the fact that the toning effected by the former does not involve any chemical change in the image, such as the substitution of one metal for another. (Au and Pt for Ag.)

The process is somewhat as follows: The picture is printed from the negative until just the faint outlines of the image are perceptible. Then it is treated with a developer, consisting, for example, of 100 parts of water, 1 part of metol (metol is a trade name for a photographic developer. Its chemical name is methyl para-amino-phenol sulphate), and 10 parts of a concentrated solution of gum (gum-water). The color of the picture varies according to the time of exposure in printing and to the time of development.

The one important disadvantage of this process is that the colors that are produced by it are very variable in nature. The tones run the gamut from bluish black to black. The developer intensifies the color of the photograph, acting on the silver salt contained in the print paper. After development the picture is washed and fixed in a bath of hypo. The gum acts as a colloid in retarding the reduction of the soluble silver salt and in mitigating the action of the physical developer.

PHOTOGRAPHIC PAPERS REQUIRING DEVELOPERS

The active principal in these papers consists of an emulsion of silver bromide or silver chlorobromide in gelatin. The paper is exposed to the action of light for a short time and the image is brought out by means of chemical developers in a manner similar to the development of negatives.

VARIATION OF THE COLOR OF THE PHOTOGRAPH BY DEVELOPMENT

The color of the picture can be varied by modifying the composition of the developer. The gelatin-silver chlorobromide papers are very much more susceptible to such toning than the gelatin-silver bromide papers. The shades run from a warm brown to a black in the latter case, while in the former greenish black tones, brown green, sepia, blood red colors are obtained by varying the time of exposure, the dilution of the developer and the duration of the development. The difference in color is due only to variation in the size of the grains of the silver, reduced by the developer.

PROCESSES OF TONING DEVELOPED PICTURES

These processes are classed as follows:

- (a) Toning by means of various metallic salts;
- (b) By sulphuration of the silver;
- (c) By fixation of coloring matters on the silver after its transformation into compounds, acting as mordants;
- (d) By the action of quinone and an alkaline bromide.

TONING BY MEANS OF VARIOUS METALLIC SALTS

This is done by the aid of a solution containing potassium ferricyanide ($K_3Fe(CN)_6$) and a metallic salt whose ferrocyanide is insoluble. The silver in the photograph acts as a reducing agent, transforming the ferricyanide into ferrocyanide ($K_4Fe(CN)_6$) and silver ferrocyanide ($Ag_2Fe(CN)_6$). The metallic salt in combination with the ferrocyanide of potassium gives a colored compound which produces the tone of the photograph.

The following conditions must be observed in order that the process prove successful:

1. The metallic salt must give a colored insoluble ferrocyanide.
2. The metallic salt must give a compound with K_3Fe

($CN)_6$, which is soluble in water or in a compound which is itself soluble in water and must be without any action on the silver of the photograph.

As silver ferrocyanide is formed by the reaction of $K_3Fe(CN)_6$ and the soluble silver salt before the toning reaction, it is necessary that the solution contain a substance, capable of dissolving the $Ag_2Fe(CN)_6$ without attacking the colored ferrocyanide so as to prevent the deposition of the orange colored $Ag_2Fe(CN)_6$ on the white spaces in the photograph. The metallic salts used for this purpose are uranium, copper, iron, molybdenum, cobalt and vanadium compounds.

TONING IN BROWN AND BLOOD RED BY MEANS OF FERROCYANIDE OF URANIUM

Two uranium ferrocyanides are known:

- A. $K_6Fe(CN)_6(UO_2)_5 + 12H_2O$.
- B. $K_2Fe(CN)_6(UO_2)_3 + 6H_2O$.

A is a fire red compound quite soluble in water, formed by the addition of a diluted uranyl salt to a concentrated solution of $K_4Fe(CN)_6$ in excess. B is a brownish red insoluble salt, formed by adding the $K_4Fe(CN)_6$ to the uranium salt solution.

In this toning process two precautions must be taken. First, the solutions should be acidified with acetic acid and second too great an excess of $K_4Fe(CN)_6$ should be avoided. If the Ur salt is in excess, then a brownish red picture is obtained; when the $K_4Fe(CN)_6$ is in excess, the first ferrocyanide of Ur (A), which is soluble, tends to form.

The nitrate of uranium is used generally. The photograph is just dipped into the bath and as the Ur ferrocyanide is somewhat soluble in water, the picture is washed for a short time only.

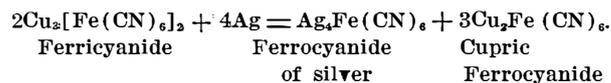
TONING IN BLUE WITH FERRIC FERROCYANIDE

When a silver picture is treated with a concentrated solution of $K_3Fe(CN)_6$, containing ferric citrate or oxalate, the silver is replaced more or less completely by ferric ferrocyanide or Prussian blue ($Fe_4[Fe(CN)_6]_3$) resulting in the formation of a blue image. The choice of the ferric salt is important. Ferric chloride ($FeCl_3$) cannot be used as it forms silver chloride. The ferric ammonia citrate is used most of all.

The ferric salt should be freed completely of all ferrous compounds, as otherwise the bath becomes blue owing to the formation of ferrous ferricyanide ($Fe_2[Fe(CN)_6]_2$), which discolors the white spaces in the photograph. The washing with water should not be prolonged for any length of time, as the alkaline action of the water tends to decolorize the toned picture.

TONING IN PURPLE BY THE AID OF CUPRIC FERROCYANIDE

For this purpose the purplish red precipitate of cupric ferrocyanide ($Cu_2[Fe(CN)_6]$), formed by mixing solutions of $K_4Fe(CN)_6$ and a cupric salt is used. The toning bath contains the latter, $K_3Fe(CN)_6$ and a solvent of the cupric ferricyanide, which forms directly in the bath. Potassium citrate ($K_3C_6H_5O_7$) is added to prevent the formation of the ferricyanide, but at the same time it does not impair the formation of the ferrocyanide which is the toning principal. The following equation shows what happens:



TONING IN REDDISH BROWN WITH MOLYBDENUM FERROCYANIDE

Ammonium molybdate, dissolved in acetic or oxalic acid, gives a reddish brown precipitate of molybdenum ferrocyanide with $K_4Fe(CN)_6$. The ferrocyanide dissolves in excess of $K_4Fe(CN)_6$ to form the double ferrocyanide of Mo and K. The Mo salt is used in a dilute solution. About 3 to 4% of $K_4Fe(CN)_6$ is added.

TONING IN VARIOUS COLOR BY USING MIXTURES OF FERROCYANIDES

The reddish uranium toned photograph can be shaded blue, more or less, by treatment with a ferric salt, which forms ferric ferrocyanide, replacing uranium ferrocyanide. The degree to which these substitutes can take place depends solely on the chemical properties of the various metallic ferrocyanides. The one that can be decomposed by a reagent can be replaced generally by the one that is not susceptible to decomposition.

Ammonia decomposes $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ but not $\text{Cu}_2\text{Fe}(\text{CN})_6$. Hence, a picture toned in iron, when treated with an ammoniacal solution of a copper salt, can be made to assume any desirable intermediate shade between blue and reddish purple by stopping the replacement process at the proper point. It is also possible to tone photographs with certain metallic ferrocyanides which cannot act on the picture directly, but which can be substituted for the original silver of the image by the interposition of another ferrocyanide.

TONING WITH FERROCYANIDES IN TWO SEPARATE BATHS

The photograph may be dipped first in a solution of $\text{K}_3\text{Fe}(\text{CN})_6$, whereat $\text{Ag} + \text{Fe}(\text{CN})_6$ is formed and the excess $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K} + \text{Fe}(\text{CN})_6$ is removed by washing. Then, any desired ferrocyanide can be formed on the image by a second immersion in a solution of the chloride of the metal. The AgCl that is precipitated and which dulls the picture can be removed by washing with a 5% hypo solution. This process admits of very general application.

TONING IN GREEN (FERROCYANIDE OF VA AND FE, AND FERROCYANIDE OF PB AND CO)

A dark green color tone can be obtained by immersing the photographs in a bath containing $\text{K}_3\text{Fe}(\text{CN})_6$, vanadium chloride, perchloride of iron, oxalic acid and potassium oxalate. A bright green tone results when two baths are used. The first contains $\text{K}_3\text{Fe}(\text{CN})_6$ and lead nitrate. This bleaches the picture forming lead ferrocyanide. Then, after the soluble lead salts are removed by washing, the picture is dipped in a solution of cobalt chloride, acidified with HCl .

TONING BY SULPHURATION OF THE SILVER

The process consists in transforming the silver of the photograph into stable sulphides of a brownish black to a sepia color. There are two methods which can be used. The first is to convert the silver directly into the sulphide and the second is to change it first into the chloride, bromide, or iodide and then into the sulphide.

TONING BY DIRECT SULPHURATION

Direct sulphuration is accomplished by the use of nascent sulphur or of the alkaline polysulphides.

Nascent sulphur may be prepared hot or cold. In the first case the photograph is treated first with formalin to prevent the gelatin from being injured by heat. The toning bath contains 50 grams of alum and 100 grams of hypo. When heated to 80°C . a reaction takes place which results in a deposition of nascent sulphur on the silver of the image. A sulphide is formed, toning the photograph. The white spots are not discolored. In using alkaline polysulphides, such as sodium bisulphide or liver of sulphur (a mixture of potassium salts and higher sulphides), it is found that discoloration does take place due to the sulphur being deposited on the white spaces in the photograph.

The process can take place in the cold by using colloidal sulphur. This is made by dissolving a mixture of $\text{Na}_2\text{S}_2\text{O}_3$ and a colloid (albumen, dextrin, gum arabic) in water and adding an acid, which decomposes the hypo, liberating the sulphur. The mixture becomes milky after a while and when this happens the picture is immersed therein. At first no change is noticed but after it has remained in the solution for 20 to 25 minutes and is then subjected to a prolonged washing, its color changes gradually to a brown and after an hour and a half

of this treatment, the tone is developed fully. The whites of the photograph are not discolored. What probably happens is that the sulphur is retained by the gelatin in the photographic paper and does not react with the silver image until the metal has been converted into Ag_2O by the oxidizing action of the wash water, while at the same time the sulphur is changed into H_2S . Then reaction takes place with formation of silver sulphide (Ag_2S). It is also likely that oxysulphides are formed and the tints that are obtained correspond to the existing proportions of the two sulphur compounds.

TONING BY INDIRECT SULPHURATION

In this process the silver is first changed into the iodide or bromide by the action of a mixture containing $\text{K}_3\text{Fe}(\text{CN})_6$ and KBr or KI . Insoluble silver ferrocyanide is formed first and $\text{K}_4\text{Fe}(\text{CN})_6$; the alkaline halide transforms the $\text{Ag}_4\text{Fe}(\text{CN})_6$ into AgBr or AgI . The soluble $\text{K}_3\text{Fe}(\text{CN})_6$ is removed by washing, and then the photograph is immersed in a solution of an alkaline sulphide. Reaction is instantaneous, a brown colored image resulting. When a halide of a metal is used, which itself will give a colored sulphide, the tone is different from that given when that substance is absent.

Cupric chloride can be used above. Then AgCl and Cu_2Cl_2 are formed. The latter remains with the AgCl and reacts to give copper sulphide (CuS) in the further treatment. It is not possible to wash out all the CuCl_2 from the picture with the result that the white spots remain discolored slightly.

SULPHURATION WITH COMPLEX SULPHIDES

Instead of the alkaline sulphides, the sulphomolybdate of ammonia or the sulphoantimoniate of soda can be used. In this case warmer tones are obtained, due very likely to the fact that a certain quantity of the metal (Mo and Sb), which is combined with the sulphur, participates in the reaction.

TONING IN VARIOUS COLORS BY MEANS OF BASIC DYES

The silver of the image is not itself capable of combining with dyestuffs directly, but it is possible to fix a certain number of basic dyes on it, provided it is first converted either into the iodide or else into an indefinite chromium compound, formed by the action of $\text{K}_3\text{Fe}(\text{CN})_6$ and chromic acid on the silver image. The picture is mordanted in this way and can be dyed permanently with basic colors. These tint the gelatin as well, but the color is removed easily by prolonged washing with water. The paper itself, however, always retains some of the dye.

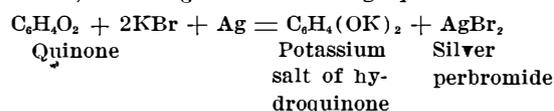
Various shades of red can be obtained with Pyronine B, Fuchsin, etc., blues with Malachite Green, Methylene Green 6B, yellows with Phosphine, Orange Acridine R, etc., etc.

The colors combined with the silver image by the mordanting action of AgI possess different properties from those in the original state. Sodium bisulphite (NaHSO_3) discolorizes malachite green, but not when it is fixed on the photograph. For this reason it is possible to decolorize the background without injuring the tone of the picture.

TONING IN COLORS BY MEANS OF QUINONE AND AN ALKALINE BROMIDE

An aqueous solution of quinone plus sour alkaline bromide will modify the color of silver images. A whole series of colors varying from a brownish black to sepia can be obtained according to the duration of the toning treatment.

What happens is not understood very clearly. It is possible that the color is due to the formation of perbromide of silver, according to the following equation:



The analysis of the toned image has not confirmed the accuracy of this equation.

