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TONING PHOTOGRAPHIC PRINTS

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This invention relates to the toning of photographic prints.

This application is, in part, a continuation of our copending application Serial No. 8,345, filed February 26, 1935.

The principal object of the present invention is to provide improved procedures for the toning of photographic prints.

An important object of the present invention is to provide procedures for toning photographic prints which avoid the disadvantages of toning processes heretofore employed.

A further object of the present invention is to provide improved procedures for toning photographic prints by the use of which toned prints of the desired color, brilliance, and clarity in detail of image can be quickly and inexpensively produced.

Another object of the present invention is to provide an improved process for toning the red color component image for multi-color photography.

Another object of the invention is to provide an improved process for toning the blue color component image for multi-color photography.

Another object of the invention is to provide an improved process for toning the yellow color component image for multi-color photography.

Another object of the invention is to provide an improved three-color printing process by which there may be produced so-called natural-color photographs which are faithful in color to the object photographed, clear in detail of image, particularly high-light detail, and brilliant in appearance.

A further object of the present invention is to provide an improved process of three-color printing which may be successfully practiced with a relatively slight degree of skill in photographic printing in order that the field of multi-color photography may be generally open to amateur photographers.

Another object of the present invention is to provide improved toning solutions for use in the practice of the above mentioned improved toning procedures.

Other objects and advantages of the invention will become apparent during the course of the following description.

In its broad aspect, our process consists in transforming the silver image on a photographic print into a latent or patent metallic salt image, while converting the metallic silver present into a compound readily removable in a suitable solvent such as "hypo", and transforming the metallic salt image into an image of a desired color having approximately the same form and gradation as the original print, the silver compound present being removed from the print either before or after the development on the print of the image of the desired color.

In its more specific aspect, our invention consists in simultaneously converting the particles of metallic silver present on a photographic print into a readily removable silver compound while depositing correspondingly distributed particles of nickel or cadmium ferrocyanide, the metallic salt thereby deposited serving as a color intermediate which is subsequently converted into a pigment of the desired color by treatment with a color precipitant. In some instances, it is desirable to deposit mixtures of the metallic salts, such as a mixture of nickel and cadmium ferrocyanide, after which the metallic ferrocyanides are converted into pigments of the desired color.

The selection of the particular metal ferrocyanide to be deposited in the first stage of our process will depend upon the final color with which the finished print is to be toned. For example, where the finished print is to be toned magenta, the print is preferably treated to transform the silver image into an image of nickel ferrocyanide which is subsequently reacted upon with a suitable color precipitant to deposit a pigment of a magenta color. If the final print is to be toned yellow, cadmium ferrocyanide may advantageously be deposited in the initial stage of the toning procedure.

The general procedure followed in the practice of the present invention involves the initial treatment of a silver photographic print in a bath containing nickel or cadmium ions and also ferricyanic acid ions, the bath containing a suitable reagent to prevent the precipitation of nickel or cadmium ferricyanide. When the silver print is immersed in a bath of the character referred to, it appears that the metallic silver present on the print effects the precipitation of nickel or cadmium ferrocyanide, the silver functioning as a reducing agent. Since the

metal ferrocyanide will be deposited only where silver particles occur on the print and to a degree corresponding to the concentration of the silver particles in any given portion of the print, the metal ferrocyanide particles will have substantially the same distribution as the original silver particles. In serving as a reducing agent to effect the precipitation of a metal ferrocyanide, the metallic silver is converted into silver oxide or hydroxide, which, by virtue of the ferricyanic acid ions present, is converted into silver ferricyanide. The silver ferricyanide may be removed from the print, as in a hypo solution, either during the first stage of treatment of the print or after the second stage of the toning operation. In either case, the print which has deposited thereon a ferrocyanide of nickel or cadmium is treated with a color precipitant to convert the metal ferrocyanide into a pigment of the desired color.

The treating bath employed in the first stage of the process comprises an aqueous medium to which has been added a soluble ferricyanide of a metal which will not form an insoluble compound with any other ion present in the treating bath; a soluble salt of nickel or cadmium; a reagent capable of preventing the precipitation in the bath of a ferricyanide of nickel or cadmium; an acid stronger than ferricyanic acid; and, preferably, an aqueous solution of formaldehyde, such as commercial formalin. Where, as in some modifications of the process, the silver content of the print is to be removed therefrom in the first-stage treatment, the treating bath should include a solvent for the silver compound formed in the treatment, which solvent is preferably an alkali metal thiosulfate, and preferably ordinary hypo solution. While the treating bath may be prepared by mixing together all of the constituent reagents at one time, it is advisable to withhold the addition of the soluble ferricyanide until just prior to the use of the treating bath.

In preparing the first-stage treating bath, we may employ any soluble ferricyanide of a metal which does not form an insoluble compound with any other ion present in the treating bath, such as potassium, sodium or ammonium ferricyanide. Our preference is for potassium ferricyanide.

Any soluble salt of nickel or cadmium may be employed in the preparation of the treating bath, such as the nitrate, sulfate, acetate, chloride, bromide, iodide or the like. Where reference is made to a "soluble" salt it is meant that the salt will provide a solution of more than one per cent. concentration at 20° C.

For the purpose of acidifying the treating bath we prefer to employ citric acid although any acid stronger than ferricyanic acid will serve, including both organic and inorganic acids, such as tartaric, acetic, oxalic, hydrochloric, nitric, or the like.

It is necessary to employ in the treating bath a reagent which will prevent the precipitation of a ferricyanide of nickel or cadmium, while permitting the precipitation of the ferrocyanide of nickel or cadmium. For this purpose we employ any freely soluble salt which in aqueous solution, in concentrations above approximately ten per cent. by weight, is a solvent for nickel and cadmium ferricyanides but which will not dissolve very appreciable amounts of the corresponding ferrocyanides. In other words, we employ a solution of a salt which is a selective solvent for the ferricyanide when both the ferrocyanide and ferricyanide are present. Thus, the salt employed serves as an inhibitor or retardant of reaction between the nickel or cadmium salt present and the soluble ferricyanide present to form an insoluble ferricyanide precipitate. In preferred practice, such inhibitor or retardant of the precipitation of an insoluble ferricyanide is potassium citrate but in place thereof we may employ any soluble salt of a so-called "fruit acid", oxalic acid or the like, such as alkali metal tartrates, oxalates, malates, succinates, benzoates, etc. In short, the salt may be any that will provide a solution which is a selective solvent for nickel or cadmium ferricyanide when the same is present with a corresponding ferrocyanide. If desired, double salts may be employed, such as potassium sodium tartrate.

After the first-stage treating bath has been prepared, the silver print to be toned is immersed therein until the silver image is thoroughly bleached. The treated print is then removed from the bath and thoroughly washed in running water until all water soluble compounds have been removed.

In some instances, it is desirable to remove the silver compound present on the treated print prior to the second stage of treatment with a color precipitant. This may be accomplished by including hypo in the original treating bath or by treating the print with a hypo solution after the first stage of treatment. Where hypo is included in the treating bath the amount of such reagent present must be controlled in order that the particles of color intermediate will be deposited on the print in substantially the same distribution as the original silver particles before the silver is removed in solution.

After the print from the first stage of the process has been washed, and the silver content removed if desired, the print is then treated with a color precipitant to convert the particles of color intermediate into a pigment of the desired color, after which the silver content of the print, if not previously removed, is then removed in a suitable solvent. As will be apparent, the color precipitant employed will depend upon the compound deposited as a color intermediate and the final color desired in the toned print.

The general procedure employed in the practice of the present invention is as outlined above but inasmuch as the commercial importance of the process is in certain cases due to special techniques in employing the general procedure, a number of specific examples of various modifications of the general process are set forth below for the sake of detailed and specific illustration of the invention.

Red-Toning

Example 1

According to this example the half-tone image of a silver photographic print is converted into an image of a magenta color which is the subtractive red or "minus green" of subtractive color printing. This example covers our preferred method of red-toning a photographic print.

In the practice of this modification of the invention a solution is first prepared by mixing 50 grams of nickel chloride, or other soluble nickel salt; 300 grams of potassium citrate or other inhibitor of reaction between a soluble nickel salt and an alkali-metal ferricyanide with the formation of a nickel ferricyanide precipitate; 30 grams of citric acid, or other acid

stronger than ferricyanic acid; preferably, 100 cc. formalin (40 per cent. aqueous formaldehyde solution); and sufficient water to make up one liter of solution. This solution may be prepared as far is advance of use as desired since it is capable of being stored over long periods. If, however, the solution is not to be stored over any substantial period the formaldehyde content may be reduced or omitted without entirely destroying the usefulness of the solution. However, it is preferred to include the formaldehyde since it not only acts as a preservative for the solution but also as a hardening agent for the gelatin on the prints treated in the solution. The formaldehyde also prevents the swelling of the gelatin emulsion on the films treated when the treating bath is used in a relatively warm surrounding atmosphere. Inasmuch as the formaldehyde does not serve its desired purpose where the treating bath is either alkaline or strongly acid, we prefer to maintain the pH value of the treating bath either at approximately 7 or only slightly on the acid side.

After the above solution has been prepared the first-stage treating bath is prepared by mixing 100 cc. of the above solution with 20 cc. of a 15 per cent. solution of potassium ferricyanide or other soluble ferricyanide of a metal which will not form an insoluble compound with any of the other ions present in the treating bath.

After the photographic print to be toned has been developed and printed in conventional manner it is thoroughly washed to remove the last trace of hypo and is then immersed in the above described treating bath for about 15 to 20 minutes, or until the silver image on the print is thoroughly bleached. The print is then washed in running water or several changes of water to remove substantially completely all water soluble compounds present. The print is then immersed in a color precipitating bath or red developer which is preferably prepared by mixing and heating together at about 50° C. for 30 minutes 30 grams of dimethylglyoxime, 250 cc. of monoethanolamine, 750 cc. of triethanolamine, and 500 cc. of an alcohol, particularly methyl or ethyl alcohol, and thereafter adding approximately 3500 cc. of water. This color precipitating bath or red developer has the advantage that it is not precipitated by water. Whereas dimethylglyoxime itself is insoluble in water it appears that in the above solution a water soluble addition compound is formed between the dimethylglyoxime and the triethanolamine. In other words, whereas a water insoluble dioxime is employed in preparing the red developer, the dioxime product present in the finished red developer is a water soluble compound.

An alternative red developer consists of 10 grams of dimethylglyoxime dissolved in 200 cc. of a mixture of 75 per cent. triethanolamine and 25 per cent. monoethanolamine and sufficient water to make up a liter of solution. This alternative color precipitating bath is prepared by heating the mixture of the two amines and the dioxime at about 100° C. for approximately 15 minutes to effect the solution of the dioxime in the mixture of amines and to effect what appears to be a reaction of the ingredients inasmuch as the solution which is initially colorless turns to a pale reddish brown color. After the heating of the ingredients as described, there is then added the amount of water necessary to make up a liter of solution.

The print is immersed in the red developer solution for about 10 minutes, or until the red color completely develops. After the color has developed the print is removed from the bath and immersed in either a 5 per cent. solution of hypo or about a 10 per cent. aqueous ammonia solution, or preferably a solution containing 2½ per cent. hypo and 1½ per cent. ammonia calculated as NH_3. This final treatment is to remove the silver salt present on the print which results in the production on the print of an extremely transparent red image. Thereafter, the red-toned print is very thoroughly washed with water.

In preparing the red developer or second-stage treating bath it is preferred to employ dimethylglyoxime in order to produce in the final tone print a pigment consisting of nickel-dimethylglyoxime. However, any dioxime may be employed in the red developer such as alpha-benzyldioxime, methylpropylglyoxime, of alpha-furyl dioxime. However, the nickel compounds of these other dioximes are not true magenta in color and, therefore, where a true magenta is desired it is preferred to employ dimethylglyoxime. While, as pointed out below in Example 2 the solvent for the dioxime employed in preparing the red developer may consist exclusively of alcohol, acetone or the like, we prefer to employ a solvent comprising a mixture of amines as described above since by the use of such solvents a more brilliant color is obtained and, where the print has been prepared on strip film, the mixed amine solvent does not shrivel the collodion backing as does a solvent such as alcohol alone.

In place of the amine mixture employed as the preferred solvent in the red developer described above, we may employ as a solvent any amine which is soluble in water and which will dissolve upward of 1/10 of 1 per cent. of the dioxime employed in the red developer. For example, monoethanolamine may be used alone as a solvent for the dioxime employed. However, this compound is a little two strongly alkaline and some high light detail is lost when the print is treated in a red developer containing this compound as the sole solvent for the dioxime. Triethanolamine may also be used alone but the results obtained therewith are not completely satisfactory. It is also possible to use tertiary amines such as tertiary butyl amine. In general, we prefer to employ aliphatic amines and to use mixtures of the same. In order to secure best results in the red developing, the developing bath must be fairly strong alkaline and in order to obtain the desired alkalinity mixtures of the amines are employed. A red developer of optimum alkalinity is obtained when the solvent for the dioxime consists of 75 per cent. tri- and 25 per cent. mono- ethanolamine. Also, diethanolamine may be used with success when mixed with 20 per cent. of either mono- or triethanolamine.

Example 2

According to this example there is obtained a final toned print of substantially the same color as produced by the preferred practice of the process described under Example 1. However, the print is somewhat less transparent and brilliant in color although the appearance of the print is substantially superior to red toned prints prepared by any of the prior art processes of which we are aware.

According to this modification of the process, we first prepare a solution of the following composition:

	Grams
Nickel nitrate	50
Potassium citrate	300
Citric acid	20
Water	500

To each 50 cc. portion of the above solution we then add a solution of the following composition:

	Grams
Potassium ferricyanide	0.4
Sodium thiosulfate	0.5
Water	50

After the treating bath has been prepared in the manner described above, the print to be toned is immersed in the bath until the silver image originally present on the print has completely disappeared and its place has been taken by an image formed by deposited particles of nickel ferrocyanide. This ordinarily requires approximately from 10 to 20 minutes. This image is only faintly visible when the print is wet and is substantially invisible when the print is dry. This, of course, is true when the print has been made upon a substantially white paper.

Inasmuch as hypo is employed in the first stage treating bath used in the present modification of the process, the silver compound formed during the treatment will be removed from the print in solution, leaving correspondingly distributed particles of nickel-ferrocyanide in place thereof.

After the print has been treated in the first-stage treating bath for the required period of time, it is removed from the bath and thoroughly washed in running water until all water soluble compounds have been removed. Generally, the print should be washed for from 15 to 20 minutes in running water.

The washed print is then contacted with a dioxime and ammonia. Preferably, the print is immersed in a solution containing a dioxime and a water-soluble or water-miscible solvent therefor. After the print has been immersed in this solution for a sufficient period of time to soak up a substantial amount of the dioxime solution, it is then removed therefrom and immersed in a relatively strong ammonia solution. For example, the print may be immersed in a solution of one gram of dimethylglyoxime dissolved in 50 cc. of methyl alcohol or other water-soluble or water-miscible solvent such as another alcohol, acetone or the like. The print is allowed to remain in such solution for about two or three minutes, or until the image in the desired intensity of color appears, and the print is thereafter withdrawn and immediately immersed in a reasonably strong aqueous solution of ammonia, such as a 5% ammonia solution. Such a solution may be prepared by mixing 1 part of commercial (28%) ammonia with 5 parts of water. The print is permitted to remain in the ammonia solution for about 5 to 10 minutes, after which the print is removed from the ammonia bath and washed thoroughly in running water for from approximately 10 to 20 minutes.

While in the present modification of the second-stage of the process it is desired to introduce the print first into the alcoholic solution of dimethylglyoxime and thereafter into an ammonia solution, it is possible to produce satisfactory results by carrying out the two operations in a single stage by adding ammonia to the alcoholic solution of dimethyl glyoxime. A suitable treating solution is as follows:

Dimethyl glyoxime	gram 1
Commercial methyl alcohol	cc 50
28% ammonia solution	cc 10

In case the print has been made on a strip film instead of on photographic paper, approximately 40 cc. of water should be added to the above solution to prevent the curling of the film of celluloid in the strip film.

Yellow Toning

Example 3

According to this example the half-tone image of a silver photographic print is converted into an image of a yellow color which is the proper primary yellow for modern three-color photographic printing. This example covers our preferred method of yellow-toning a photographic print.

In the practice of this modification of the invention we first prepare a solution of 40 grams of cadmium nitrate or other soluble cadmium salt in 200 cc. of water. This solution may be referred to as Solution A. We then prepare a solution, which may be termed Solution B, by mixing 300 grams of potassium citrate, or other inhibitor or retardant of the precipitation of cadmium ferricyanide in the treating bath; 30 grams of citric acid, or an equivalent amount of other acid stronger than ferricyanic acid; 100 cc. of formalin; and sufficient water to make up 800 cc. of solution.

Solution A is then added to Solution B slowly and with rapid agitation to prevent precipitation of cadmium citrate. 100 cc. of the resulting solution are then mixed with 20 cc. of a 15 per cent. solution of potassium ferricyanide or other soluble ferricyanide. The resulting solution is then employed as the first-stage treating bath.

The print to be toned yellow is immersed in the treating bath for approximately 15 minutes. The print is then removed from the treating bath and rinsed for approximately one minute in water in a washing tray. While the print is out of the first-stage treating bath there is added thereto 10 cc. of a 20 per cent. hypo solution. The print is then immersed in the thus treating first-stage bath for approximately from 3 to 5 minutes, the tray containing the treating bath being rocked vigorously during this time. The print is then removed from the treating bath, which is discarded, and returned to the washing tray where it is rinsed for say one minute. The rinsed print is then immersed in a 5 per cent. solution of hypo for about one minute, or until the print is well bleached and the image on the print is pure white. The print is then washed very thoroughly. This treatment completes the first-stage treatment and as a result thereof the original silver image on the photographic print has been replaced by an image of cadmium ferrocyanide.

In the second stage of treatment the cadmium ferrocyanide image is converted into an image of cadmium sulfide which, as is well known, is primary yellow in color. This result is preferably accomplished by immersing the print for from one to two minutes in a yellow developer containing 7 per cent. sodium bicarbonate, 5 per-cent. sodium sulfide and 88 per cent. water. The sodium bicarbonate is employed as a buffer to keep down the pH value of the solution. In place of sodium bicarbonate there may be em-

ployed other acid salts, such as sodium bisulfate, or a weak acid. In place of sodium sulfide, any other soluble sulfides, such as ammonium polysulfide, may be used but we have found that sodium sulfide gives the best results. In the yellow developer prepared as described above there will be present a small amount of free hydrogen sulfide. If desired, a water solution of hydrogen sulfide might be employed as the yellow developer in place of the solution described above but the results obtained therewith are not so satisfactory as where the preferred yellow developer is employed.

After the print has been immersed in the yellow developer until the image of the desired intensity of color has been obtained the print is washed thoroughly. If, after washing, any yellow stains appear in the portions of the print which should be white, these stains can be cleared up by immersing the print of a 1 per cent. hydrochloric acid solution for about one to 2 minutes. In the event that the yellow color on the print is too intense, the intensity of the yellow may be reduced by immersing the print for say 10 to 15 minutes in a 1 per cent. hydrochloric acid solution to dissolve out some of the cadmium sulfide present.

In commercial practice some of the users of the above described yellow developer have objected to the strong odor thereof. We have found that this objection may be overcome by adding approximately 160 cc. of triethanolamine to each liter of the yellow developer solution. The free hydrogen sulfide apparently is taken up to form triethanolamine sulfide which has only a very slight odor which is not objectionable. Moreover, by the addition of the triethanolamine to the yellow developer referred to a denser yellow color in the shadow portions of the toned pictures is obtained. Ordinarily, complete color precipitaton is effected in this modified yellow developer in about 5 minutes.

In the above described procedure of yellow-toning, there is first prepared a first-stage treating bath in which the print is immersed, following which hypo is added to the bath, the print then rinsed and again treated with hypo before being immersed in the second-stage treating bath containing a soluble sulfide. If there be added to the first-stage treating bath approximately 3.5 grams of potassium thiocyanate (or any other alkali-metal thiocyanate, including ammonium thiocyanate) in each 100 cc. of treating bath, the print after being treated in this bath merely requires washing and subsequent treatment in the second-stage sulfide solution to effect yellow-toning, and does not require any treatment with hypo or the like. In other words, we may merely use the first-stage treating bath described above, with potassium thiocyanate added to it, immerse the print to be toned in such bath, subsequently wash the print, and thereafter effect yellow-toning in the yellow developer containing a soluble sulfide. As will be apparent, this simplifies our preferred yellow-toning procedure quite substantially. Moreover, we may, if desired, use an alkali-metal thiocyanate in place of hypo in other modifications of the process.

Example 4

According to this example the silver image of a photographic print is replaced by an image of nickel ferrocyanide by employing the first-stage treatment described above in Example 2. The resulting print is then thoroughly washed with water and contacted with free chlorine. This is preferably effected by immersing the washed print in a solution containing free chlorine, such as a solution of bleaching powder to which an acid, preferably acetic acid, has been added.

A treating solution of the following composition has been found suitable for use in the practice of the above referred to modification of the process:

	Cubic centimeters
Water	100
Bleaching powder solution (88 grams available chlorine per litre of water)	12
1:4 acetic acid	25

(Where reference is made to 1:4 acetic acid it is, of course, meant that the acid is of a concentration resulting from mixing 1 part of commercial acetic acid with 4 parts of water. Similar designations of concentration are hereinafter used in the same sense.)

The print to be toned is immersed in a solution of the above composition for about 5 to 10 minutes, after which it is removed and washed thoroughly in running water for from 10 to 20 minutes.

Example 5

In this modification of the process a photographic print is first treated to replace the metallic silver present with cadmium ferrocyanide. This may be accomplished by employing the first-stage treating bath described above in Example 2 but having a soluble cadmium salt substituted for the soluble nickel salt in the first-stage treating bath described in Example 2. After the print has been treated to replace the silver image with an image of cadium ferrocyanide the print is thoroughly washed in running water for from 10 to 20 minutes, and is immersed in an aqueous solution of sodium sulfide for several minutes. The concentration of the sodium sulfide solution may vary considerably but we have found that a solution containing from 1 to 5 per cent. sodium sulfide by weight is the most satisfactory. As will be apparent, the lower the concentration of sodium sulfide in the solution, the slower will be the development of the yellow color in the print. We have found that it is advisable to use relatively low concentrations of sodium sulfide in the treating solution and permit the print to remain in the solution for a longer period. The print ordinarily should be immersed in the treating bath for from 2 to 10 minutes. Thereafter, the print is removed from the bath and thoroughly washed in running water.

BLUE TONING

Example 6

According to this example the half-tone image of a silver photographic print is converted into an image of a blue color which is the primary blue of color photography. This example covers our preferred method of blue-toning a photographic print.

According to this modification of our process, we prepare the first-stage treating bath by adding a soluble ferricyanide to an aqueous solution whose constituent reagents are a soluble nickel salt, an inhibitor of the precipitation of nickel ferricyanide, an acid stronger than ferricyanic acid, and, preferably, formaldehyde.

In preferred practice, we prepare the first-stage treating bath by adding 20 cc. of a 15 per cent.

solution of potassium ferricyanide to 100 cc. of a solution of the following composition:

Nickel chloride	grams	50
Potassium citrate	do	300
Citric acid	do	30
Formalin	cc	100

Sufficient water to make up 1 litre of solution.

The print to be toned is immersed in the first-stage treating bath for about 15 to 20 minutes or until the image is thoroughly bleached. The print is then removed from the treating bath and washed very thoroughly. The washed print is then immersed in a 5 per cent. solution of ferric chloride or other soluble ferric salt, such as ferric nitrate or ferric sulfate, for about 5 minutes or until a bluish-green color develops in the print. The print is then removed from this bath, and, without washing, is immersed in a 1:3 hydrochloric acid solution for about 1 minute to intensify the greenish color. Thereafter, the print is washed for about 5 minutes in running water. The washed print is placed in a bath containing 5 per cent. hypo for about one minute to develop a blue-green color. During this treatment the silver salt present on the print is removed. The thus treated print is then washed in water containing a minute trace of acid, such as one-hundredth of 1 per cent. of hydrochloric or sulfuric acid. The washing water should contain sufficient acid to maintain the pH value well below 7, say about 5.

In the above second-stage treatment with a soluble iron salt, the silver ferricyanide, which is present on the print with the nickel ferrocyanide, apparently reacts with the iron salt such as ferric chloride to produce iron ferrocyanide and say silver chloride. This reaction occurs slowly but if hydrochloric acid is added, as described above, the reaction proceeds materially faster. It appears that when the hydrochloric acid is added, the silver ferricyanide oxidizes the hydrochloric acid, yielding chlorine, and the silver ferricyanide is reduced to silver ferrocyanide which reacts with the iron salt present to yield iron ferrocyanide. The hypo solution subsequently added dissolves out the silver salt, say silver chloride, and also any unconverted silver ferricyanide.

It is possible to substitute for the soluble ferric salts in the second-stage treatment, soluble ferrous salts, such as the sulfate or chloride, and the desired blue-green color develops very rapidly. Consequently, it is not absolutely necessary to treat the print with a hydrochloric acid solution after treatment with a soluble ferrous salt. However, it is not advisable to eliminate the hydrochloric acid treatment. When using soluble ferrous salts a small amount of a yellow precipitate forms in the film, which is probably insoluble iron hydroxide, and the use of the hydrochloric acid treatment is advisable in order to remove this compound from the print.

Example 7

This example is a modification of the process described in the preceding example and produces a final toned print of substantially the same color as that produced in accordance with the preceding example.

In this embodiment of the invention the print to be toned is immersed for about 15 minutes in a treating bath made up by adding 20 cc. of a 15 per cent. solution of potassium ferricyanide to 100 cc. of a solution made up by mixing (slowly and with rapid agitation) 40 grams of cadmium nitrate dissolved in 200 cc. of water with a solution of 300 grams of potassium citrate, 30 grams of citric acid, and 100 cc. of formalin in sufficient water to make up 800 cc. After treatment of the print in this first-stage treating bath for about 15 minutes, the print is rinsed in another tray for about one minute. While the print is out of the first-stage treating bath, 10 cc. of a 20 per cent. hypo solution are added to the bath. The print is returned to the bath and permitted to remain immersed therein for from 3 to 5 minutes, the tray containing the bath being rocked vigorously during this time. The print is then removed from the bath and washed. Thereafter, the print is then immersed in a 5 per cent. solution of hypo for about one minute until the print is well bleached and the image is substantially pure white. The print is then washed thoroughly. This treatment completes the first stage of treatment and results in the removal of the original silver content of the film with the replacement of an image of cadmium ferrocyanide for the original silver image.

The white image on the print is then converted to a blue image of the desired color by treatment of the print with a soluble iron salt. This treatment may consist in treating the print with a soluble ferrous salt, followed by washing, or may consist in the treatment of the print with a soluble ferric salt, followed by treatment with a hydrochloric acid solution, after which the print is washed. For example, the print may be immersed for about 5 minutes in a 5 per cent. solution of ferric chloride after which the print, without washing, is placed in a tray of 1:3 hydrochloric acid for one minute following which the print is washed for about 5 minutes in running water, or, preferably, in an acidified wash water having a pH of about 5.

Example 8

In this modification of the process the silver image on a photographic print is replaced with an image of nickel ferrocyanide and this may be accomplished by treatment of the print in a first-stage treating bath of the composition described above in Example 2. The resulting print is then immersed in an acidified solution of a soluble ferric salt, such as ferric nitrate or ferric chloride. A treating solution of the following composition has been found suitable:

Ferric nitrate	grams	5
1:1 hydrochloric acid	cc	5
Water	cc	100

The print is left in the treating solution for from 5 to 10 minutes, after which it is withdrawn and thoroughly washed in running water. The resulting print is of a green color, the original silver image having been replaced by a green image. This green image is converted into an image of a blue color by immersing the green-toned print in a dilute solution of an alkali-metal thiosulfate, such as a dilute hypo solution. A solution of suitable concentration can be prepared by dissolving one gram of sodium thiosulfate in 100 cc. of water. The print is left in this solution for several minutes until an image of the desired intensity of color appears in the print.

If the print resulting from the foregoing treatment is "muddy" in appearance and the highlight detail is not clear, the print after washing may be immersed in a solution of an alkali metal salt of a so-called "fruit acid", such as a 10 per

cent. potassium citrate solution, in which solution the print is left for from a few seconds to one minute, after which the print is withdrawn from the solution and then immediately washed thoroughly in running water.

MIXED COLOR TONING

Example 9

By this modification, green toning is obtained in the final print.

In this embodiment of the invention the silver image on a photographic print is first replaced with an image of nickel ferrocyanide and this may be accomplished by subjecting the print to the first-stage treatment described above in Example 2. The thus treated print is then thoroughly washed and is immersed in an acidified solution of a soluble ferric salt, such as ferric nitrate of ferric chloride. Free acid should be present in the solution and any acid is suitable for the purpose, hydrochloric acid being preferred. A second-stage treating bath of the following composition is satisfactory for green toning:

Ferric nitrate	grams	5
1:1 hydrochloric acid	cc.	5
Water	cc.	100

The print is left in the treating solution for from 5 to 10 minutes, after which it is withdrawn and thoroughly washed in running water.

Example 10

By this modification of the process, a toning in flesh color is obtained.

In the practice of this embodiment of the invention, the silver image of a photographic print is first replaced with an image of nickel ferrocyanide and this may be accomplished by the first-stage treating operation described above in Example 2.

The washed print from the first stage of the process is treated with an ammoniacal solution of alpha-benzyldioxime in alcohol. The treating solution may have the following composition:

Alpha-benzyldioxime	gram	0.5
Commercial methyl alcohol	cc.	50
28 per cent ammonia solution	cc.	10

The print is left in the treating solution until the image in the desired intensity of color appears on the print after which the print is removed from the treating bath and thoroughly washed with running water.

Example 11

According to this example a print is toned in a brown color.

The print to be toned is first treated to replace the silver image with an image of nickel ferrocyanide and this may be accomplished by treating the print in accordance with first-stage operation described above in Example 2. The print is then thoroughly washed and immersed in an aqueous solution of an alkali metal sulfide, such as a 5 per cent. sodium sulfide solution. After the image has appeared on the print in the desired intensity of color, the print is removed from the bath and thoroughly washed with running water.

Example 12

By the present modification, the final print under treatment is toned a violet color.

In accordance with this example, the print to be toned is first treated to replace the silver image originally present with an image of nickel ferrocyanide. This may be accomplished by subjecting the print to the first-stage treatment described above in Example 2. Thereafter, the print is thoroughly washed.

The washed print from the first stage of the process is first immersed in an acidified aqueous solution of a water-soluble iron (ferric) salt, such as ferric nitrate or ferric chloride. A treating solution of the following composition has been found to be satisfactory:

Ferric nitrate	grams	5
1:1 hydrochloric acid	cc.	5
Water	cc.	500

The print is treated in such a solution for about 1 to 2 minutes. The print is then withdrawn from the bath and washed in running water for a short period. The thus treated print is then immersed in an ammoniacal solution of a dioxime in alcohol or other water-soluble or water-miscible solvent. A treating solution of the following composition has been found to be suitable:

Dimethyl glyoxime	gram	1
Commercial methyl alcohol	cc.	50
28 per cent. ammonia solution	cc.	10

The print is permitted to remain in the last mentioned bath until an image of the desired intensity of color is obtained, after which the print is withdrawn from the bath and washed with water.

As a result of the foregoing treatment the final print is toned a violet color. The particular shade of violet can be varied throughout substantially the complete range from red to blue by varying the amount of the iron salt deposited on the print in the first operation of the second stage of the process as described in the present example. As will be apparent, the larger the amount of iron salt deposited on the print, the bluer will be the violet color of the toned print and the lesser the amount of iron salt deposited on the print, the redder will be the violet in the final toned print.

Example 13

By this modification of the invention a photographic print may be toned in an orange color.

During the first stage of the process the original silver particles in the print are replaced with approximately equal parts of nickel ferrocyanide and cadmium ferrocyanide in the manner described above. Thereafter, the print is treated in accordance with Example 2 set forth above to produce a red pigment from the nickel ferrocyanide present. Thereafter, the print is thoroughly washed and is then treated according to Example 6 to convert the cadmium ferrocyanide into a yellow pigment. Thereafter, the print is thoroughly washed in running water.

As will be apparent, by varying the proportions of nickel ferrocyanide and cadmium ferrocyanide deposited on the print in the first stage of the process, the particular shade of orange produced in the final print can be varied considerably, the color range extending from a very reddish orange to a very yellowish orange.

Example 14

By this modification the final print is toned a yellowish green color.

During the first stage of the process both nickel ferrocyanide and cadmium ferrocyanide are deposited in the manner described above in the preceding example. The resulting print is then thoroughly washed with water. Thereafter, the

washed print is treated with a substantially neutral solution of a soluble iron (ferric) salt, such as ferric nitrate or ferric chloride. A 5 per cent. solution of ferric nitrate will be found to be satisfactory. The print is permitted to remain in this treating solution for about 2 minutes and, thereafter, is withdrawn and thoroughly washed in running water. The print is then immersed for from 2 to 10 minutes in an aqueous solution of an alkali-metal sulfide, such as a solution of from 1 to 5 per cent. sodium sulfide.

MULTI-COLOR TONING

Example 15

According to this modification of the process, a photographic print is first toned in a single color in the manner described above and, thereafter, portions of the toned print are treated with a color modifying agent which will react with the pigment present in the toned print to produce a pigment of a different color.

In the preferred practice of this modification, the print is first treated in accordance with Examples 1 or 2 to replace the original silver image with a nickel-dioxime image.

Any portion of the red-toned print may be changed to a green color by applying an acidified solution of a soluble ferric salt.

Any portion of the red-toned print may be changed to a blue color by treating the print with a soluble ferric salt until the treated portion of the print has developed a good green color, after which the print is washed and the same portion of the print is treated with a hypo solution.

Any portion of the red-toned print may be changed to a brown color by applying to that portion an acidified aqueous solution of a soluble ferric salt. After a purplish green color has developed, the print is washed with water and then dipped into an ammonia solution, and the print thereafter washed.

Any portion of the red-toned print may be changed to a yellow color by applying to that portion of the print a saturated solution of chlorine gas in water containing about 2 per cent of hydrochloric acid.

If the chlorine gas solution is diluted with approximately 5 parts of water, an orange color will be developed instead of the yellow color produced with the stronger solution.

Example 16

This modification is concerned with the toning of bi-pack films, such as Dupac films.

In the practice of this modification, an object is photographed in the usual manner with bi-pack film and positives are produced from the two films in the usual manner. Both positives are then treated in a first-stage treating bath of the character described above in Examples 1 and 6. After the prints have been washed, the positive made from the negative which was the back film of the original bi-pack film is subjected to the second-stage treatment described above under Example 6 to tone the positive in the desired blue-green color. The positive made from the negative which was the front film of the original bi-pack film is then treated in the preferred red developer described above under Example 1, with the exception that the dimethylglyoxime of such red developer is substituted by alphabenzyldioxime. Thereafter, the print is further treated as described in Example 1 to remove the silver present, following which the print is washed in the usual manner.

THREE-COLOR PRINTING FROM COLOR SEPARATION NEGATIVES

The greatest commercial importance of the present invention resides in its applicability to the preparation of natural-color photographic prints prepared from color separation negatives. Accordingly, there is described in the following example a complete method of producing natural-color photographs from color separation negatives by the use of which final prints of the highest photographic excellence yet obtained in the art may be easily and inexpensively produced.

Example 17

Color separation negatives are prepared in the usual manner. The negatives should be well exposed and developed to a lower degree of contrast than is customary in black-and-white work. The gamma of the color separation negatives produced should be from .8 to 1.2.

Starting with a set of negatives, black-and-white positive prints are made on strip film. In making these black-and-white positives it is essential that the three positives have the same scale of graduation and identical densities in the neutral portions of the subject. In other words, gray areas such as shadows on white objects should appear identical in the positives. It is best to include in the original subject a so-called "step-wedge" which is a series of gray squares ranging from white to black. In printing the positives then it is only necessary to reproduce this step-wedge identically in each to insure proper color balance in the finished color print.

These positives are developed in a developer chosen to give a soft but brilliant image without too much contrast. From very "contrasty" negatives soft prints may be obtained by using a metol or amidol developer. Starting with negatives which are too soft or flat, vigorous prints may be made by using a pure hydroquinone developer. Experienced photographic workers will understand proper methods of obtaining the softly brilliant prints demanded by color printing processes.

The prints after development are fixed preferably in a metabisulfite-hypo fixer. The acid fixers containing alum should not be used because they form a film or scum of alumina on the surface of the prints which interferes with the toning reactions. Fixing should be continued for about 15 minutes after which the prints are thoroughly washed with water.

During fixing or early in the washing, the film strips from the paper backing. The paper backing is thrown away and the films handled unsupported thereafter. In washing these films it is recommended that they be placed one at a time in a tray of clean water, transferred one at a time to another tray of water, the first tray emptied and refilled and the films transferred back to it, and this process to be continued until the films have been transferred through about seven changes of water. This method of washing is positive, consumes a minimum of time, and obviates the possibility of tearing or kinking the films during washing.

After the three positive prints have been prepared in the manner described above, the positives to be toned blue-green and magenta are transferred to a tray containing a treating bath prepared by mixing 20 cc. of a 15 per cent. solu-

tion of potassium ferricyanide with 100 cc. of a solution of the following composition:

Nickel chloride	grams	50
Potassium citrate	do	300
Citric acid	do	30
Formalin	cc	100

Sufficient water to make up 1 liter.

The tray containing the above treating bath is rocked to expel air bubbles from under the films and to insure rapid and uniform immersion of the films. The tray is then set aside until the first-stage of treatment has been completed, which takes from 15 to 20 minutes.

The positive print or film to be toned yellow is then immersed in a yellow-toning treating bath. This is prepared by dissolving 40 grams of cadmium nitrate in 200 cc. of water, adding the resulting solution slowly and with rapid agitation to a solution made up of 300 grams of potassium citrate, 30 grams of citric acid, 100 cc. of formalin, and sufficient water to make up 800 cc. of solution, to each 100 cc. portion of which solution is then aded 20 cc. of a 15 per cent. solution of potassium ferricyanide. The tray containing this solution in which is immersed the print to be toned yellow is then set aside.

When the prints to be toned blue-green and magenta have been thoroughly bleached, the print to be toned magenta is removed from the first-stage treating bath and placed in another tray containing fresh water and the film washed by changing the water in the tray about four times, each time making certain that the film floats free of the bottom of the tray so as not to entrap chemicals beneath it. After washing the print to be toned magenta is introduced into another tray and there is added sufficient amount of a red developer to cover the film, the tray then being set aside. The red developer preferably is prepared by mixing and heating together at about 50° C., for about 30 minutes, 30 grams of dimethylglyoxime, 750 cc. of triethanolamine, 250 cc. of monoethanolamine and 500 cc. of methyl or ethyl alcohol. Thereafter, there is added about 3500 cc. of water to make up the final developing solution. After about 10 minutes the red developer is poured off the film immersed therein and the film is then treated with a 25 per cent. solution of hypo for about 5 minutes. Thereafter, the film is washed with three or four changes of water, following which the film is immersed for a few seconds in a 1 per cent. solution of acetic acid and washed again with two or three changes of water.

The print to be toned blue-green is removed from the first-stage treating bath after about 5 minutes and thoroughly washed. There is then added to a tray containing the washed print sufficient of a 5 per cent. solution of ferric chloride to cover the film. After about 3 minutes, this solution is poured off and the film flushed with water. Thereupon, the film is covered with a dilute solution of hydrochloric acid. In about a minute, this solution is poured off and another portion of dilute hydrochloric acid added and allowed to remain on the film for a few minutes. This solution is poured off and the film washed with about five changes of water and immersed in a 25 per cent. solution of hypo for about 5 minutes, after which it is washed with five changes of water.

After the print which is to be toned yellow has been immersed for about 15 minutes in the yellow toning treating bath, the solution is poured off into a graduate. About 20 per cent. by volume of a 25 per cent. solution of hypo is added to the graduate, the solution well mixed and poured back on to the film. After about 2 minutes the solution is discarded and the film washed once or twice and then immersed in a 5 per cent. solution of hypo, after which the film is washed with about ten changes of water. Thereupon, there is poured on to the film a solution of the following composition:

	Per cent
Sodium bicarbonate	7
Sodium sulphide	5
Water	88

After about one minute this solution is poured off and the film washed with five changes of water.

The three prints which have been toned magenta, blue-green, and yellow are then ready for mounting, which is preferably carried out as follows: A piece of gelatin-coated white paper is soaked in water for 2 or 3 minutes and is laid on a clean surface with the gelatin side up. The strip film bearing the yellow image is laid on this paper, gelatin side down, and squeegeed firmly into place. The magenta print is then superimposed on the yellow print, moved into approximate register, squeegeed lightly, pushed into accurate register and squeegeed firmly down into place. The blue toned film is then superimposed, registered and squeegeed into place. This completes the preparation of the color print.

The print is permitted to dry somewhat after the registration has been checked and found to be satisfactory. It is then secured to a smooth, rigid board, preferably by means of gummed tape. The tape should overlap the print by a margin of about ¼ inch and the remaining width of the tape pressed firmly to the surface of the mounting board. As the print dries this tape will hold the print absolutely flat and prevent any tendency to cockle or buckle around the edges. The print is preferably permitted to dry over night, after which may be removed from the board by cutting around the edges with a sharp knife. The print is then trimmed to the desired size and shape and mounted permanently on a stiff card or backing board.

While we have described in detail the preferred embodiments of our invention and numerous modifications thereof, it will be apparent that the details of procedure may be variously modified without departing from the spirit of the invention or the scope of the subjoined claims.

We claim:

1. In a process of toning a silver photographic print in which the silver image is replaced at least in part with a cadmium sulfide image, the improvement which comprises immersing the print in an aqueous treating bath whose constituent ingredients include a soluble cadmium salt, a soluble ferricyanide, and an hydroxy aliphatic acid capable of forming a complex metal-acid ion, removing from the print the silver compound formed by dissolving the same in a solution of a solvent reagent selected from the group consisting of soluble thiosulfates and thiocyanates, washing the resulting print, and immersing the washed print in a solution containing a soluble sulfide.

2. In a process of toning a silver photographic print in which the silver image is replaced at least in part with a cadmium sulfide image, the improvement which comprises immersing the

print in an aqueous treating bath whose constituent ingredients include a soluble cadmium salt, a soluble ferricyanide, and a hydroxy aliphatic acid salt which in solution is a selective solvent of cadmium ferricyanide when the same is present with cadmium ferrocyanide, removing the silver compound formed by dissolving the same in a solution of a solvent reagent selected from the group consisting of soluble thiosulfates and thiocyanates, washing the resulting print, and immersing the washed print in a solution containing a soluble sulfide.

3. In a process of toning a silver photographic print in which the silver image is replaced at least in part with a cadmium sulfide image, the improvement which comprises immersing the print in an aqueous treating bath whose constituent ingredients include a soluble cadmium salt, a soluble ferricyanide, and a soluble salt of an organic acid which in solution is a selective solvent of cadmium ferricyanide when the same is present with cadmium ferrocyanide selected from the group consisting of tartrates, citrates, oxalates, malates, succinates and benzoates, removing the silver compound formed by dissolving the same in a solution of a solvent reagent selected from the group consisting of soluble thiosulfates and thiocyanates, washing the resulting print, and immersing the washed print in a solution containing a soluble sulfide.

4. In a process of toning a silver photographic print in which the silver image is replaced at least in part with a cadmium sulfide image, the improvement which comprises immersing the print in an aqueous treating bath whose constituent ingredients include a soluble cadmium salt, a soluble ferricyanide, a soluble salt of a hydroxy aliphatic acid capable of forming a complex metal-acid ion, removing the resulting print from the treating bath, washing the print with water, immersing the print in a bath of a reagent selected from the group consisting of soluble thiosulfates and thiocyanates, washing the print and immersing the washed print in a solution containing a soluble sulfide.

5. In a process of toning a silver photographic print in which the silver image is replaced at least in part with a cadmium sulfide image, the improvement which comprises immersing the print in an aqueous treating bath whose constituent ingredients include a soluble cadmium salt, a soluble ferricyanide, a soluble salt of a hydroxy aliphatic acid capable of forming a complex metal-acid ion, and a reagent selected from the group consisting of soluble thiosulfates and thiocyanates, removing the resulting print from the treating bath, washing the print with water, and immersing the washed print in a solution containing a soluble sulfide.

6. In a process of toning a silver photographic print in which the silver image is replaced at least in part with a cadmium sulfide image, the improvement which comprises immersing the print in an aqueous treating bath whose constituent ingredients include a soluble cadmium salt, a soluble ferricyanide, and a soluble citrate, removing the resulting print from the treating bath, washing the print with water, immersing the print in a solution of a reagent selected from the group consisting of soluble thiosulfates and thiocyanates, washing the resulting print, and immersing the washed print in a solution containing a soluble sulfide.

7. In a process of toning a silver photographic print in which the silver image is replaced at least in part with a cadmium sulfide image, the improvement which comprises immersing the print in an aqueous treating bath whose constituent ingredients include a soluble cadmium salt, a soluble ferricyanide, a soluble citrate, and a reagent selected from the group consisting of soluble thiosulfates and thiocyanates, washing the resulting print, and immersing the washed print in a solution containing a soluble sulfide.

8. The process of yellow-toning a silver photographic print which comprises immersing the print in a treating bath whose constituent ingredients include a soluble cadmium salt, an alkali-metal ferricyanide, a salt of an hydroxy aliphatic acid which in solution is a selective solvent of cadmium ferricyanide when the same is present with cadmium ferrocyanide, an acid stronger than ferricyanic acid, formaldehyde and water, removing the print from the treating bath and adding to such bath a thiosulfate solution, returning the print to the resulting bath, washing the resulting print, immersing the washed print in a thiosulfate solution, washing the resulting print, immersing the washed print in a solution containing a soluble sulfide, and washing the resulting print.

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