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COLOR PHOTOGRAPHY

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The present invention relates to new and useful improvements in color photography, relating more particularly to a photographic process in which an initial image is reproduced in terms of a blue color and to a blue colored photographic image resulting from such a process.

It is well known in the art of color photography that a plurality of colored images each of which is reproduced in a primary color, such as blue, yellow or magenta, may be assembled, superimposed in registry, or otherwise combined to produce a completed colored image which covers the full color range of the visible spectrum. These initial colored images must be carefully selected as to color value and intensity so that, when combined, a balanced colored print is produced. The blue photographic print of the present invention may be used in any desired method of assembly or combining of the separate color images utilized to produce such a finished colored print. The other initial colored images also used for this purpose, may be produced by any known process which provides colors suitable for use with the blue color prints herein disclosed.

It is one object of the present invention to provide an improved blue photographic print and a simple, effective and convenient method for the production thereof, the method being readily controlled to produce a blue color of predetermined color values and light transmitting properties.

It is another object of the invention to provide a process for producing a blue photographic print which includes a conversion of an initial conventional photographic black-and-white image to a blue image which reproduces the gradations and tones of the initial image and which is lightfast and capable of repeated satisfactory exhibitions or uses particularly photographic projections.

Another object of the invention is the provision of a process for producing a blue photographic print in which an initial black-and-white image may be bleached and at the same time oxidized to produce an oxidized bleached image in a single operation or step; and to provide such a process in which stain or reaction products of the bleaching and oxidizing reactions are readily removed from the emulsion.

A further object of the invention is to provide a process in which the blue colored image may be simply, quickly and conveniently produced preferably in but two operations or steps, namely, a combined bleaching and oxidizing operation and a combined clearing and color forming operation.

Still another object of the invention is to produce a blue image which is free from color blocking, that is, the present blue image may be employed with other colored images for forming a completed color photograph and without causing shades of black in an undesired manner particularly at the intensely colored portions of the photograph. In this regard, the present invention overcomes a problem long present in the art; for former blues have tended to produce shades of black instead of correctly reproducing shades of deep blue, purple, deep red, and other deep colors, thereby greatly lowering the quality of the completed color photograph. The present process produces a blue image capable of correctly representing such colors and also one which, at the same time, correctly represents light blues or light colors containing blue, such for example as shades of green.

Other objects and advantages of the invention will become apparent during the course of the following description and of the appended claims forming a part hereof.

According to the present invention, an initial photographic image is first produced and is thereafter converted by chemical reactions into a blue colored image reproducing the initial image. In preparing this initial image, known photographic materials may be employed as well as photographic procedure and technique within the purview of a skilled photographer. To illustrate, a developed black-and-white metallic image, such as a developed silver image, may be produced in a film, plate or other suitable image recording medium and any instance in which metallic silver has been precipitated in gelatin films, agar-agar films or the like has produced satisfactory initial images.

In producing such initial images in the selected image recording medium, the usual photoghrapic control factors are considered. Thus, suitable exposure times should be employed for the particular film or paper employed, as well as suitable developers, time of development, short stop baths, and other photographic operations and materials known to skilled photographers in making satisfactory black-and-white photographs. As pointed out above, however, the blue image of the present invention is a reproduction of the initial black-and-white image. Thus, the density of the initial black-and-white image is an important factor in determining the density of the blue image derived therefrom. Accordingly, careful control of the density of the initial image by the usual photographic control factors, mentioned above, should be effected in order that a blue image of the desired density may result from the present process.

As a result of numerous experiments, I have

found that the following image recording mediums and developers produced therewith have produced satisfactory initial images for purposes of the present invention. It should be expressly understood, however, that these mediums and developers are given by way of illustration and not of limitation. For producing the initial black-and-white image of the present invention on film, the positive films such as those produced by the Eastman Kodak Company have been found satisfactory, and in developing the image on this medium, the developer known as "D–76" of the Eastman Kodak Company is recommended, as is the developer known at "Panthermic 777" of the Defender Photo Supply Company. In producing such an initial image in direct positive printing paper of the Eastman Kodak Company, the developer known as "D–88" of the Eastman Kodak Company is recommended. In case ordinary projection printing papers are employed, such as "Velour Black" of the Defender Photo Supply Company, any suitable developer may be employed, such as "M. Q." developers or "55–D" of the Defender Photo Supply Company. In producing an initial image for the present invention in stripping papers, the stripping paper known as the Chromatone stripping paper of the Defender Photo Supply Company is particularly recommended. The developer for this stripping paper should be "55–D," referred to above, if the negative from which the initial image is made is a normal negative, that is, in case this negative possesses no abnormal contrast or subnormal contrast. In case the negative is a "hard" negative, that is, in case it possesses more contrast than normal or more contrast than is desired, a so-called "soft" developer should be employed such as the developer known as "59–D" of the Defender Photo Supply Company. In case the negative from which the initial image of the present invention is made, is a "soft" negative, that is, one which is subnormal in contrast characteristics, a "hard" developer should be employed such as the developer known as "15–D" of the Defender Photo Supply Company. In case the stripping paper known as "Kodalith" is employed, a very soft developer should be used since this particular stripping paper produces an image which tends to possess too much contrast for most uses of the present invention. In this regard, it will be appreciated that even if the initial image of the present invention is formed in a photographic medium other than a stripping film, that a hard developer should be employed in case the negative, from which the image is made, is a soft negative; and, on the other hand, a soft developer should be employed in case the negative is a "hard" negative. Development of the initial image of the present invention may be accomplished in any suitable manner such as in trays or in a tank. Standard photographic practice is utilized in the development operation, such as conventional washing operations.

For the preparation of the blue-and-white image, according to the present invention, the initial black-and-white image is first converted into a water insoluble complex iron cyanide image. The conversion of an initial black-and-white image to form such a reaction product image is known in the art as "bleaching" and the image resulting from such an operation is known as a "bleached" image. The bleaching operation of the present invention is accomplished by immersing the emulsion containing the initial black-and-white image in a bath containing complex iron cyanide ions and also containing an additional suitable oxidizing agent. A ferricyanide is recommended as the complex iron cyanide for this bleaching bath and a permanganate is recommended as this additional oxidizing agent, although it will be understood that other complex iron cyanides may be employed as well as other suitable additional oxidizing agents. For instance, the following bleaching bath has produced satisfactory results:

Potassium permanganate	gms	2
Potassium ferricyanide	gms	10
Sodium bicarbonate	gm	1
Water to make	cc	250

The sodium bicarbonate is added to the bath to act as a stabilizer and, more expressly, to act as a buffering agent. The bath may be used without sodium bicarbonate but its useful life is considerably shortened. Furthermore, it has been found that solutions maintained at pH values such as bicarbonate solutions possess have the characteristic of more rapidly penetrating the gelatin of the film and of being more readily removed by washing. It will be understood that other suitable buffering agents may be employed and that such agents are known to skilled chemists. The emulsion containing the initial black-and-white image is left in the bleaching bath until the reaction has gone to completion. Howeve, the time of such immersion can be determined by visual observation since the black-and-white image is converted to a reaction product image which is otherwise a faithful reproduction of the initial black-and-white image. This reaction product image is of a distinctly different color than the initial black-and-white image. For example, it may comprise orange colored, silver ferricyanide. However, in case a permanganate is used as the oxidizing agent, the emulsion after the bleaching step will be stained a brownish color resulting from the presence of manganese dioxide which is produced by the oxidizing action of the permanganate. This stain is removed from the emulsion in later steps of my process in the manner fully explained hereinafter, and may interfere with the aforementioned visual observation. In this case, the time of immersion to complete the reaction is determined by a simple experiment and the emulsion is left in the bath until the reaction is completed. For the particular bleaching bath expressly set forth above, this time of immersion is about thirty seconds to about three minutes, the average time being about one and one-half minutes.

After the initial image has been converted or bleached, it is next thoroughly washed in order to remove surplus reagents (which may remain in the emulsion) such as the bleaching solution. Such washing may be accomplished in flowing water or by means of a series of washing operations in accordance with recognized photographic practice. The time of such washing or the extent thereof may be readily determined since the bleaching solution containing the permanganate is reddish purple or magenta in color. Thus, the emulsion should be washed until all traces of reddish or pink solutions are removed, that is, until the wash water is substantially clear.

In view of the foregoing, it will be appreciated that the bleached image, according to the present invention, consists of an oxidized complex radical consisting of iron and a cyanide radical in chemical combination with the metal which

made up the initial black-and-white image. Thus, if the initial image were a silver image, the bleached image consists of silver in combination with an oxidized complex iron cyanide, and if a ferricyanide were employed in the bleaching bath, this image will consist of silver ferricyanide.

While it is preferable that the initial image be converted into a complex iron cyanide image and also oxidized in a single operation, as described above, it is possible to first convert the image into an image containing a reduced iron cyanide radical and then to oxidize this image in a separate oxidizing step. For example, the initial image may be immersed in a bath containing a ferricyanide without an oxidizing agent to form a bleached image consisting of a ferrocyanide in combination with the metal making up the initial image, such as silver ferrocyanide. Thereafter, this image may be immersed in a suitable oxidizing agent and converted into a silver ferricyanide image.

In addition, it will be appreciated that other bleaching agents may be employed rather than the complex iron cyanide compound, expressly referred to above, a number of which are well known in the art. For instance, the initial black-and-white image may be immersed in a solution containing a halide, chromates or other compounds reactive with the metal forming the initial black-and-white image to produce a reaction product image. This reaction product image may then be immersed in a bath containing a complex iron cyanide to form an image consisting of the metal of the initial image combined with a complex iron cyanide. However, it will be understood that this complex iron cyanide image should be oxidized to produce an oxidized complex iron cyanide radical in combination with the metal either in a separate oxidizing operation or at the bleaching operation, in the manner indicated above, so that the final bleached image, according to the present invention, will consist of the metal forming the initial image combined with an oxidized iron cyanide complex radical, such, for example, as silver ferricyanide.

The black-and-white image after having been bleached and washed, is placed in a solution containing ferrous ions. Since this bleached image is made up of a metal in combination with a ferricyanide, it will be seen that the ferrous ions react with the image to produce an image consisting of ferroferricyanide, also known as Turnbull's blue. This reaction is permitted to go to completion which may be determined by the appearance of the blue colored image.

In addition to ferrous ions, the blue forming baths of the present invention also contain a reducing agent. This reducing agent attacks the reaction products resulting from the oxidizing action of the oxidizing agent in the bleaching bath. For example, where the oxidizing agent employed in the bleaching bath was a permanganate, the manganese dioxide resulting from the oxidizing action of the permanganate is attacked by the reducing agent in the blue forming bath and is rendered water soluble so that said manganese dioxide may be removed from the emulsion and thereby clear the emulsion of the brownish stain resulting from manganese dioxide. While a number of reducing agents suitable for such use will occur to a skilled chemist, the following have produced satisfactory results and are therefore recommended: Oxalic acid, tartaric acid, citric acid, an alkaline solution of hydrogen peroxide, and a chromous or chromic compound. While a reducing agent, especially the particular reducing agents mentioned, are preferable for removing the manganese dioxide from the emulsion, other substances which react with manganese dioxide to form a soluble reaction product may be employed. For instance, sulfuric acid can be used since soluble manganese sulfate would be formed.

The concentration of the ferrous compound in my blue forming baths is not particularly critical although it has been found that a relatively high concentration of ferrous ions has produced a blue image in a shorter period of time and is therefore more satisfactory, although the image may be left in the bath containing a relatively weak concentration of ferrous ions until the reaction goes to completion. The concentration of the reducing agent or other reagent employed to form a soluble manganese compound, should be made suitable for the particular reagent employed. This concentration should be determined so that said reagent will react with the reaction products in the emulsion but will not excessively attack or reduce the metallic ferricyanide image which is being converted into the blue ferroferricyanide image, as more fully explained hereinafter. In case oxalic, tartaric or citric acids are employed, saturated aqueous solutions may be used. I have found, however, from a number of experiments that in case these acids are employed, a minimum concentration of approximately four atoms of each acid for each atom of the ferrous compounds employed is satisfactory for most purposes. In case chromous or chromic compounds are employed as a reducing agent, I have found that weaker concentrations may be employed and that a minimum concentration of approximately two atoms of the ferrous compounds for each atom of the chromous or chromic salts used may be utilized.

By way of illustration but not of limitation, the following express blue forming baths are given:

Example No. 1

Ferrous ammonium sulfate	gms	2
Potassium bromide	gm	½
Chromium sulfate	gm	½
Sodium bisulfite	gms	2
Water to make	cc	250

Example No. 2

Ferrous sulfate	gms	2
Potassium bromide	gm	½
Citric acid	gms	2
Water to make	cc	250

The purpose of the bisulfate in the blue forming bath is to provide hydrogen ions in the solution so that basic iron salts, such as ferrous hydroxide, will not precipitate from the solution. Thus, other agents suitable to provide hydrogen ions and thus keep ferrous ions in the solution may be employed, such as sulfuric acid itself or other suitable acids. The pH value of the solution should be maintained at less than approximately 4.3 since ferrous salts precipitate from a more basic solution. This pH value also prevents undesired precipitation of ferric as well as ferrous compounds.

In case the reducing agent or other agent employed to react with the maganese dioxide is an acid, it will be appreciated that the bisulfate may be dispensed with. In this event, the acid fulfills a double purpose, first to provide the blue

forming bath with the proper pH value, and second to attack the manganese dioxide to form a soluble manganese compound for removing stain. The citric acid of the blue forming bath numbered 2 hereinbefore serves such a double purpose.

It will be observed that in the foregoing baths the ferrous compound and the manganese dioxide removing reagents were combined in a single bath. It should be understood, however, that this reagent may comprise the principal ingredient of a separate bath. In this case, the manganese dioxide or other reaction products resulting from the oxidation during the bleaching step are reacted to render them soluble and removed from the emulsion prior to the formation of the blue ferroferricyanide. For example, the washed and bleached image, that is, the image consisting of silver ferricyanide, may be immersed in a bath containing any one of the aforesaid reducing agents, such as an aqueous bath containing a saturated solution of oxalic, citric or tartaric acids or a solution containing 2 grams of chromous sulfate for each 250 cc. of solution. The film, after it is cleared of the reaction products, may then be washed and immersed in a blue forming bath which is similar to the above described blue forming bath except that the reducing agent is removed therefrom. For example, such an image may be immersed in a bath made up as follows:

Ferrous sulfate	gms	2
Potassium bromide	gm	½
Sodium bisulfate	gms	2

In case such a separate bath containing the reducing agents is employed, it is desirable to wash the emulsion before it is immersed in the blue forming bath containing the ferrous ions. However, a complete wash at this point is not utterly necessary.

After the blue forming reaction has been permitted to go to completion to provide a blue image consisting of ferroferricyanide, the emulsion is immersed in a plain hypo bath, that is, an aqueous solution of sodium thiosulfate. It is desirable to add a small quantity of a preservative to the hypo solution to prevent bacterial decomposition of the thiosulfate. Chloroform is satisfactory for this purpose and about .05% by volume has proved to be a satisfactory concentration. By immersion in this hypo bath, the light sensitive compounds contained in the emulsion, which were not reacted to form the initial black-and-white image, are removed and dissolved so that a cleared blue-and-white image reproducing the initial black-and-white image results. The emulsion is then washed and dried in accordance with recognized photographic practice to form the completed blue-and-white photographic print of the present invention.

Instead of employing a separate hypo bath in the manner explained above, sodium thiosulfate may be added to the blue forming bath, if desired. However, this procedure is not particularly recommended inasmuch as the life of the combined hypo and blue forming bath is relatively short and, consequently, the bath should be freshly prepared before use. The reason for the deterioration of such a combined bath appears to be due to the precipitation of free sulfur from the bath which might be prevented by the addition of a sulfite to the bath. However, the addition of such a sulfite to the combined blue forming and hypo bath has been found to interfere with the production of a desired blue image due to the reduction of the ferricyanide with the liberation of SO_2 and resultant loss of the colored image. However, such a combined bath can be used and approximately two grams of sodium thiosulfate should be added for each 250 cc. of any one of the foregoing blue forming baths. For example, the following combined hypo and blue forming bath could be employed:

Ferrous sulfate	gms	2
Sodium thiosulfate (Also a reducing agent for M_nO_2)	gms	2
Boric acid	gms	2
Potassium bromide	gm	1
Water to make	cc	250

It will be understood that instead of boric acid, citric acid, oxalic or tartaric acids could be employed and that chromium compounds could be used in place of boric, citric, tartaric or oxalic acids. In the latter event, one gram of a chromous or chromium compound is recommended. It is also pointed out that in this combined hypo and blue forming bath, the thiosulfate acts as a reducing agent for the manganese dioxide thereby fulfilling the double purpose of dissolving the excess unreacted silver salts from the emulsion and attacking the manganese dioxide for removing the brown manganese dioxide stain from the emulsion.

It will be noted from the foregoing examples of my blue forming bath that each of these baths contains a soluble halide such as potassium bromide. The presence of such a halide in the bath is particularly recommended because I have found that it is desirable to depress the ionic concentration of silver in the blue forming bath. Since silver halides are very insoluble, it will be appreciated that the introduction of a soluble halide provides a simple means of so depressing the ionic concentration of silver. However, any suitable agent for accomplishing this purpose may be employed and such agents will readily occur to a skilled chemist. The reason for depressing the ionic concentration of silver in the blue forming bath will be appreciated after consideration of the following chemical equations which represent the reactions taking place in the blue forming bath to form the blue image. However, it should be understood that this reasoning and these equations constitute my opinion only, in this regard.

(1) $Ag_3[Fe(CN)_6]$ (Silver ferricyanide) + $3FeSO_4$ (Ferrous sulfate) $\xrightarrow{(Ag^+)}$ (Silver ion)

$Ag_4[Fe(CN)_6]$ (Silver ferrocyanide) + $Fe_2(SO_4)_3$ (Ferric sulfate)

(2) $3Ag_4[Fe(CN)_6]$ (Silver ferrocyanide) + $2Fe_2(SO_4)_3$ (Ferric sulfate) $\longleftrightarrow$

$Fe_4[Fe(CN)_6]_3$ (Ferriferrocyanide) + $6Ag_2SO_4$ (Silver sulfate)

(3) $2Ag_3[Fe(CN)_6]$ (Silver ferricyanide) + $3FeSO_4$ (Ferrous sulfate) $\longrightarrow$

$3Ag_2SO_4$ (Silver sulfate) + $Fe_4[Fe(CN)_6]_3$ (Ferro-ferricyanide)

(4) Ag_2SO_4 (Silver sulfate) $\xrightarrow[H_2O]{\longleftrightarrow}$ $2Ag^+ + SO_4^{--}$ $\downarrow$ (halide)

Ag halide

$\downarrow$ R^+Ha^- (halide of potassium, iodine, bromine)

$AgHa + R_2SO_4$ $\downarrow$

In view of the foregoing equations, it will be understood that the presence of free ions of silver in the blue forming bath tends to form silver ferrocyanide (Equation 1) and also ferriferrocyanide (Equation 2). This is a side reaction taking place at the same time as the principal reaction illustrated by Equation 3. Ferriferrocyanide or Prussian blue, produced by this side reaction, is not as satisfactory a blue color producing compound as ferroferricyanide or Turnbull's blue produced by the principal reaction. Moreover, the side reaction indicated by Equations 1 and 2 renders the blue producing reaction difficult to control since it causes the blue image to consist of a mixture of Prussian blue and Turnbull's blue thereby making a desired or proper blue color value of the image difficult to secure, and making the blue images difficult to reproduce with uniform results as to color value and density. In order to restrict the reaction to the one illustrated in Equation 3, it is necessary to depress the ionic concentration of silver further than the $Ag_4[Fe(CN)_6]$ of Equation 1 will do. The presence of a halide in the solution accomplishes this result, as indicated in Equation 4, since silver halides are much more insoluble than silver ferrocyanide

$(Ag_4[Fe(CN)]_6)$

Thus, a blue forming solution containing a halide, or in which the ionic concentration of silver is otherwise depressed, produces a single reaction, the reaction indicated by Equation 3, and thereby forms a blue image consisting solely of ferroferricyanide or Turnbull's blue. Such an image possesses better color values. It may be controlled and brought to a desired density, and, it is reproduceable with uniform color values and densities since it is made up of a single compound instead of a mixture of compounds, and its blue forming reaction is not complicated by side reactions most difficult to control.

The blue images of the present invention have been found to be free from color blocking, that is, the present blue image may be employed with other colored images for forming a completed color photograph without causing shades of black in an undesired manner, particularly at the intensely colored portions of the photograph. For example, the present blue correctly reproduces shades of deep blue, purple, deep red and other deep colors without giving the appearance of a black or a grayish tint to such colors which appearance is known in the art as color blocking. This characteristic of the present blue to avoid such blocking comprises an important feature of the present invention and is believed to be brought about for the following reasons although it is to be understood that these reasons merely comprise my explanation; and, whatever the explanation, the result has been observed. It is thought that the reducing agent, in addition to its function of removing reaction products resulting from the oxidation in the bleaching step also fulfills another function. This additional function is to reduce or attack the silver ferricyanide bleached image at the heavier portions thereof. Thus, the heavier portions of the silver ferricyanide image are reduced somewhat before the ferrous ions react with such portions to form the blue ferroferricyanide. It will be appreciated that a strong reducing agent could not be employed, since all of the silver ferricyanide would be reduced thereby removing the blue producing compound. Such a strong reducing agent would produce, chiefly, ferrocyanide which does not provide a satisfactory blue image. Accordingly, the reducing power of the reducing agent is very important and the reducing agent should be so selected that it will reduce the silver ferricyanide at a relatively slow rate as compared with the rate of reaction with the ferrous ions with the silver ferricyanide. The reducing agents mentioned expressly hereinbefore appear to have the desired reducing characteristics. Also, it will be appreciated in view of this explanation that the concentration of the reducing agent, with respect to the concentration of the ferrous ions, is important. As explained above, I have found that a minimum concentration of one atom of a chromous or chromic salt, when these compounds are employed as a reducing agent, for each atom of the ferrous compound appears to produce the desired ratio. Also, I have found that approximately four atoms of oxalic, tartaric or citric acids for each atom of the ferrous compound appears to provide the correct ratio when these acids are employed as the reducing agent. However, it will be understood that these ratios and these compounds are given by way of express example only and that other reducing agents and other ratios may be employed to secure the desired effect by simple experiments well within the purview of a skilled chemist, provided that the inventive concept of the present invention is followed.

I claim:

1. A method of producing a blue photographic image from an initial silver photographic image which comprises reacting said initial image in a single operation with a complex iron cyanide and also with an oxidizing agent, in an amount sufficient to form silver ferricyanide to form a bleached oxidized image containing silver ferricyanide, and reacting said bleached image with a soluble ferrous iron compound to form a substantially water insoluble blue colored image containing ferroferricyanide.

2. A method of producing a blue photographic image from an initial developed silver image which comprises reacting said initial image with a water soluble complex iron cyanide and with an oxidizing agent in an amount sufficient to form an image consisting of silver ferricyanide, subjecting the emulsion containing the last said image to the action of a soluble ferrous iron compound to form a substantially water insoluble blue compound consisting substantially entirely of ferroferricyanide, subjecting said emulsion to the action of a reagent reactive with reaction products of said bleaching and oxidizing operations to render said reaction products soluble, and clearing said emulsion by wetting it with a solvent for said reaction products and with a solvent adapted to remove all other compounds deposited in the emulsion which form no part of said blue color producing compound.

3. A method of producing a blue photographic image from an initial black-and-white silver image which comprises reacting said initial image with a water soluble complex iron cyanide and with an oxidizing agent in a sufficient amount to form a reaction product image consisting of silver ferricyanide, subjecting the emulsion containing said reaction product image to the action of a soluble ferrous iron compound to form a substantially water insoluble blue compound consisting substantially entirely of ferroferricyanide, subjecting said emulsion to the action of a reducing agent adapted to render reaction prod-

ucts of said bleaching and oxidizing operations soluble without reducing to an undesired extent a ferricyanide radical, and clearing said emulsion by wetting it with a solvent for said reaction products.

4. A method of producing a blue photographic image from an initial black-and-white developed silver image which comprises subjecting the emulsion containing said initial image to the action of a complex iron cyanide and to the action of a permanganate to produce a bleached image containing silver ferricyanide, thereafter subjecting said emulsion to the action of a reducing agent adapted to reduce the manganese containing reaction products resulting from the oxidizing action of said permanganate to render said reaction products water soluble, and subjecting said emulsion to the action of an aqueous solution of a ferrous iron compound to produce a blue colored image comprising ferroferricyanide and also for removing said water soluble reaction products from the emulsion.

5. The method as defined in claim 4 and further characterized in that the emulsion, after being subjected to the action of the aqueous solution of a ferrous iron compound, is additionally treated by subjecting it to the action of a selected solvent adapted to dissolve and remove from the emulsion all remaining compounds which form no part of the blue color producing compounds.

6. The method as defined in claim 4 and further characterized in that the reducing agent is selected from the group consisting of oxalic acid, citric acid, tartaric acid, hydrogen peroxide in an acidic solution, and a chromium containing compound in which the valence of chromium does not exceed three.

7. A method of producing a blue photographic image from an initial black-and-white silver photographic image which comprises immersing the emulsion containing said initial image in a bath containing a ferricyanide and an oxidizing agent in a sufficient amount to produce a bleached image comprising silver ferricyanide, thereafter immersing said emulsion in an aqueous solution containing a water soluble ferrous iron compound and a reducing agent adapted to reduce the reaction products of the said oxidizing operation to render said products water soluble but which does not extensively reduce the ferricyanide radical, thereby forming a blue colored image comprising ferroferricyanide and also removing the aforesaid reaction products from the emulsion.

8. The method as defined in claim 7 characterized in that the oxidizing agent is a permanganate, and in that the reducing agent is a chromium salt in which chromium is a positive element and has a valance not exceeding three.

9. The method as defined in claim 7 in which the oxidizing agent is a permanganate, in which the reducing agent is a chromous salt, and in which the emulsion is immersed in a hypo solution for clearing the blue image.

10. A method of producing a blue photographic image from an initial developed silver image which comprises immersing the emulsion containing said initial image in a bath containing a permanganate and a ferricyanide to form an image consisting of silver ferricyanide and thereafter immersing said emulsion in an aqueous bath containing ferrous ions to form a blue image consisting of ferroferricyanide, said second bath also containing a reducing agent selected from the group consisting of oxalic acid, citric acid, tartaric acid, hydrogen peroxide in acidic solution, and a chromium containing compound in which the valence of chromium does not exceed three, whereby the manganese dioxide resulting from the oxidizing action of said permanganate is reduced and made water soluble so that it is dissolved and removed from the emulsion.

11. A method of producing a blue photographic image from an initial developed silver image which comprises subjecting said initial image to the action of an oxidizing agent and a ferricyanide to form a reaction product image consisting of silver ferricyanide, and thereafter immersing said emulsion in an aqueous bath containing ferrous ions to form a blue image consisting of ferroferricyanide, said second bath also containing a reducing agent adapted to reduce said silver ferricyanide at a predetermined rate as compared with the rate of reaction of said ferrous ions with said silver ferricyanide compound, so that the relatively light portions of said reaction product image are substantially completely converted to said blue ferroferricyanide and a portion of the relatively dense portions of said reaction product image are reduced while the remainder of said dense portions are converted into said blue ferroferricyanide.

12. A method of producing a blue photographic image from an initial developed silver image which comprises immersing the emulsion containing said initial image in a bath containing a permanganate and a ferricyanide to produce a reaction product image consisting of silver ferricyanide, and thereafter immersing said emulsion in an aqueous bath containing ferrous ions to form a blue image consisting of ferroferricyanide, said second bath containing a reducing agent selected from the group consisting of oxalic acid, citric acid, tartaric acid, hydrogen peroxide in an acidic solution and a chromium containing compound in which the valence of chromium does not exceed three, the concentration of said reducing agent being so determined that the relatively light portions of said reaction product image are substantially completely converted into said blue ferroferricyanide by said ferrous ions and a portion of the relatively dense portions of said reaction product image are reduced by said reducing agent while the unreduced remainder of said dense portions are converted into said blue ferroferricyanide.

13. The method as defined in claim 12 characterized in that the reducing agent is a chromium compound in which chromium has a valence not exceeding three, and in which the minimum concentration of said chromium compound is approximately two atoms of ferrous compound for each atom of said chromium compound.

14. The method as defined in claim 12 characterized in that the reducing agent is oxalic acid and in which the minimum concentration of the oxalic acid is approximately four atoms of oxalic acid to one atom of the ferrous compound.

15. The method as defined in claim 12 characterized in that the reducing agent is citric acid and in which the minimum concentration of the citric acid is approximately four atoms of citric acid to one atom of the ferrous compound.

16. The method as defined in claim 12 characterized in that the reducing agent is tartaric acid and in which the minimum concentration of the tartaric acid is approximately four atoms of tartaric acid to one atom of the ferrous compound.

17. The method as defined in claim 2 characterized in that the emulsion while subjected to the action of the soluble iron compound is also subjected to the action of an agent for depressing concentration of the ions of the metal forming the initial image.

18. The method as defined in claim 10 characterized in that the aqueous bath containing the ferrous ions and the reducing agent also contains a soluble halide thereby depressing the ionic concentration of silver in said bath.

ALBERT L. BUNTING.

Certificate of Correction

Patent No. 2,341,079. February 8, 1944.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, first column, line 28, strike out the formula and insert instead the following—

$$(Ag_4[Fe(CN)_6])$$

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of June, A. D. 1944.

[SEAL]

LESLIE FRAZER,
Acting Commissioner of Patents.