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PROCESS FOR INTENSIFYING SILVER PHOTOGRAPHIC IMAGES

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8 Claims. (Cl. 95—88)

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This invention relates to photography. More particularly it relates to a process for intensifying weak silver photographic images. Still more particularly it relates to a process for intensifying silver photographic images by toning the silver image with a plurality of polyvalent metal salt solutions.

In processes of color photography, for example, it is desirable to increase the optical density of silver images for various purposes and particularly for printing purposes. Thus, it is often desirable to obtain stable images which have densities 8 to 10 times the density of the original silver image. Uranium toned images have been proposed for this purpose, but uranium salts are not available in large quantities for this use. Iron toned images show a large degree of intensification but are low in optical density to the blue light normally used for printing.

An object of this invention is to provide a process for providing toned silver images. Another object is to provide such a process that will produce stable toned silver images of high density. Yet another object is to provide such a process which utilizes available chemical raw materials.

A further object is to provide such a process which can be carried out in a continuous manner without careful observation and involved technical procedures. Still further objects will be apparent from the following description of the invention.

It has been found that controllable increases, up to ten-fold, and even higher in density or contrast of photographic silver images can be obtained by treating such an image in a water-permeable colloid layer of an exposed and developed photographic element, e. g., a film or paper, with an aqueous solution containing ferricyanide ions and one or more cations taken from the group consisting of lead, zinc, silver, mercury, copper, nickel, cobalt and cadmium followed by treatment with a second aqueous solution containing one or more inorganic polyvalent metal cations that form relatively water-insoluble ferrocyanide compounds and one or more anions taken from the group consisting of blue-light-absorbing complex oxide ions of hexavalent chromium.

The lead, zinc, silver, mercury, copper, nickel, cobalt or cadmium ions in the first bath are cations which form relatively insoluble ferrocyanide and chromate compounds. Best results are obtainable with lead ions. Hence, it is preferred to use lead ions alone or in preponderating amounts when zinc or other ions are present.

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When silver images are toned by the procedure just described, the resulting toned images markedly are increased in optical density to blue-light and, depending on the particular cations in the second solution, to all visible wave lengths.

In the preferred aspect of the invention the silver image in the exposed and developed photographic element is first converted into a lead ferrocyanide image by treating the silver image with a lead ferricyanide bleach bath, for instance, an aqueous solution containing a water-soluble, inorganic lead salt, an alkali metal ferricyanide and an alkali metal bromide. The photographic element is then washed with water and the white image of $Pb_2Fe(CN)_6$ is converted through a metathetical reaction into a mixed image composed of yellow lead chromate and blue ferric ferrocyanide by treating it in an iron chromate toning bath, e. g., an aqueous solution containing a soluble ferric salt and an alkali metal chromate or dichromate and resulting element is then washed. Chromates and dichromates are essentially equivalent in this invention since these two ionic species are always in equilibrium in aqueous solutions in proportions dependent on the pH.

The invention will be further illustrated but is not intended to be limited by the following examples.

Example I

A photographic film consisting of a colorless cellulose triacetate film base having a thickness of approximately 0.0055 inch provided with a thin gelatin sublayer was coated with a gelatino silver bromiodide emulsion which contained about 96.0 mols of AgBr per 3.4 mols of AgI to produce a coating weight of approximately 9 mg. silver halide and 67 mg. of gelatin per square decimeter. The resulting photographic film was exposed in an intensity-scale sensitometer (see C. E. K. Mees "The Theory of the Photographic Process," MacMillan 1948, pp. 607-623) utilizing a simulated daylight source and developed for five minutes in the following developer at 68° F.:

Water	-----cc	975.0
Mono-methyl-p-aminophenol, sulfuric acid salt	-----gm	0.8
Sodium sulfite, anhydrous	-----gm	90.0
Hydroquinone	-----gm	1.0
Borax	-----gm	3.0
Potassium bromide	-----gm	0.1

After fixing, washing and drying, the silver image was observed to be of very low optical density. On measurement by an electronic

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densitometer it was found that the maximum diffuse density was 0.16. Then this silver image was bleached for five minutes at 68° F. in a solution of the composition:

Water	ml	700.0
Acetic acid, glacial	ml	30.0
Lead nitrate	gms	16.0
Potassium ferricyanide, dissolved in 100 cc. H ₂ O	gms	8.0
Potassium bromide, dissolved in 100 cc. H ₂ O	gms	2.9
Water to make 1.0 liter.		

The resulting bleached film was washed for five minutes with agitation in water at 58° F., and then treated for ten minutes at 68° F. in a solution of the following composition:

Water	ml	700.0
Ferric nitrate 9H ₂ O	gms	40.0
Potassium dichromate	gms	3.8
Potassium ferricyanide	gms	7.5
Water to make 1.0 liter.		

The resulting film was washed for 5 minutes and dried and it was found upon measurement that the diffuse optical density to blue light (400–490) millimicrons transmitted by a filter was increased from 0.16 to 2.0. The density of the intensified image was equivalent to that of a normal negative film having a Weston exposure speed of approximately 40, and the gamma was approximately 1.1 to blue light. To green and red light the gammas were approximately 0.8 and 1.1, respectively.

A control film made from the same emulsion but having a coating weight of 85 mg. silver halide per square decimeter produced a silver image characteristic of light sensitive film having Weston speed 30 and gamma 0.6 when developed for five minutes in the above developer and fixed, washed and dried.

Example II

A photographic film consisting of a cellulose triacetate film base having a thickness of about 0.0051 inch and being tinted with a dye to have antihalation properties was coated with a green-blind, red-sensitive gelatino silver bromiodide photosensitive emulsion containing a water-soluble yellow filter dye of the type described in Example 2 of Gaspar U. S. Patent 2,274,782 to produce a coating weight of approximately 70 mg. silver halide and 70 mg. gelatin per square decimeter. Over the latter emulsion layer was coated a water-sensitive stripping layer composed of 8 mg. of 88% hydrolyzed polyvinyl acetate having a medium viscosity mixed with 4 mg. of 99% hydrolyzed polyvinyl acetate of medium viscosity per square decimeter. The stripping layer was coated with a green-sensitive gelatino silver bromiodide photosensitive emulsion to produce a coating weight of approximately 70 mg. silver halide and 70 mg. gelatin per square decimeter. A water-sensitive stripping layer having a coating weight of 21 mg. per square decimeter and composed of medium viscosity 88% hydrolyzed polyvinyl acetate was coated onto the latter green-sensitive gelatin silver bromiodide layer. The upper stripping layer was coated with a blue-sensitive gelatino silver bromiodide emulsion of the type and having a coating weight as set forth in Example I. A suitable dye for the green-blind emulsion is 1,1'-diethyl-2,4-carbo-cyanine iodide and for the green-sensitive one is 1,1'-diethyl-2,2'-cyanine iodide.

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The film element just described was exposed to a multicolor scene and after wetting it with water at a temperature of 80° F. the outer blue and green record emulsion layers were successively transferred to separate blank films consisting of a cellulose acetate film base having a layer of gelatin at pH_s at coating weight of 70 mg. per square decimeter. After drying the separate films bearing the red and green records they were developed to gamma 0.75 in a developer solution having the composition given in Example I, fixed, washed and dried. The remaining blue record film (bearing the low coating weight emulsion) was developed to completion in a developer of the same composition given in Example I, fixed, washed and dried. The weak silver image of the blue record emulsion was bleached to completion at 68° F. in a solution of the following composition:

Water	ml	700.0
Acetic acid, glacial	ml	30.0
Lead nitrate	gms	16.0
Potassium ferricyanide, dissolved in 100 cc. H ₂ O	gms	8.0
Potassium bromide, dissolved in 100 cc. H ₂ O	gms	2.9
Water to make 1.0 liter.		

washed for a period of five minutes in cold water with agitation and then toned to gamma approximately 0.8 to green light in a solution of the following composition:

Water	ml	700.0
Ferric nitrate 9H ₂ O	gms	40.0
Potassium dichromate	gms	3.8
Potassium ferricyanide	gms	7.5
Water to make 1.0 liter.		

The three separate film elements containing the color separation records were then separately printed into the appropriate layers of a multilayer color print film of the type described in the Journal of the Society of Motion Picture and Television Engineers, November 1950, pp. 455–476. This exposed multilayer film was then processed to a color reproduction as described in said journal.

The presence of ferricyanide ions in the second or toning solution is not essential but does produce a higher degree of intensification. The mechanism of this effect is not known with certainty. A magenta or green light-absorbing dye or pigment e. g. Anthraquinone Rubine R conc. (Colour Index—1091), Pontacyl Carmine 6B Extra (Colour Index—57) and Pontacyl Rubine Extra conc. (Colour Index—178) could be placed in the final rinse to at least partially neutralize the green color of the mixed image of lead chromate and ferric ferrocyanide. The dyes just mentioned are described in the 1951 Technical Manual and Yearbook of the American Association of Textile Chemists and Colorists, vol. 27, Howes Publishing Co., Inc., New York, N. Y.

Example III

The process set forth in Example I was repeated except that the film had the silver halide coating weight increased to 17 mg. per square decimeter. This film had a maximum diffuse optical density of 0.32 when developed to a silver image. When intensified by the procedure of Example I but replacing the iron salt in the toner by 20 gms. uranyl nitrate per liter, the maximum diffuse density was increased to 2.13 to blue light. In the place of the lead nitrate in the fore-

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going first or bleach bath there may be substituted various other soluble lead salts. Suitable additional salts include lead acetate, lead bromide, lead chloride, lead formate, lead lactate, and lead citrate. The proportion of the lead salts in the aqueous bleach bath may vary from 1 to 25 grams or more per liter.

Similarly, in place of the acetic acid used in the first bath of the foregoing examples there may be substituted various other acids in equivalent amount. Suitable acids which can be substituted or admixed with the acetic acid are formic acid, hydrochloric acid, citric acid, nitric acid, glycollic acid and lactic acid. The amount of acid can be varied over fairly wide limits depending on the desired degree of acidity and/or sequestration. Buffering salts such as alkali acetates, formates, lactates, citrates, etc. can be added to the solution for pH regulation in the preferred range of 1 to 6.

Likewise, in place of the potassium ferricyanide used in the foregoing first bath, or in addition thereto, one may substitute other equivalent ferricyanides including ammonium ferricyanide, sodium ferricyanide, and mixed ferricyanides of such cations. The ferricyanide compounds can be used in amounts varying from 0.5 to 25 grams per liter of solution.

All or part of the potassium bromide can be omitted or substituted by other agents which form insoluble silver salts, such as sodium and ammonium chlorides and bromides can be used in amounts of 1 to 25 grams per liter of solution.

Suitable zinc and cadmium salts which can be substituted in equivalent amount for all or part of the lead salts include zinc and cadmium acetates, zinc and cadmium sulfates, zinc and cadmium nitrates, and zinc and cadmium chlorides. The corresponding soluble salts of silver, mercury, copper, nickel, and cobalt can also be used in equivalent amounts.

With regard to the second toning bath various other water-soluble chromate or dichromate salts can be substituted for all or part of the potassium dichromate. Among such other salts are: sodium and ammonium chromates and dichromates. The proportion of the chromate or dichromate salts may vary from 0.5 to 25 grams per liter.

In place of the ferric salt or uranyl salt used in the second bath one may substitute other polyvalent salts containing in solution the following cations that produce insoluble ferrocyanide compounds: VO^{++} , Cu^{++} , Ag^{+} , Co^{++} , Mn^{++} , Hg^{++} , Ni^{++} . These insoluble ferrocyanide compounds are usually colored but need not necessarily be colored. For example, a colorless ferrocyanide compound co-precipitated with lead chromate can add to the printing density of the latter by making the path of blue light through the film more devious. Furthermore, the presence of a white pigment in the film can lessen "grain" patterns by its diffusing and scattering action on light.

The amount of the intensification of the image can be controlled by varying the amount of time the film element is in the first and second baths. The first bath essentially is a bleach bath and the second a toning bath. The time of treatment in these baths may vary from 1 to 20 minutes. The temperatures may vary in the baths but, in general, should be maintained from 50 to 80° F. For constant uniform results, it is best to bleach to completion in the first bath and then tone the bleached image in the second bath. The bath

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of Example I above is a fast-acting toner. A practical slow-acting toner solution is as follows.

Water	cc.	700
Acetic acid, glacial	cc.	3
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	gms.	3
K_2CrO_4 , dissolved in 100 cc. water	gm.	1
Water to make 1.0 liter.		

As evident from this solution and Example I, the molar concentration of ferric salt may vary from 0.01 to 0.10.

In some films the gelatin coating weight is insufficient to prevent loss of lead chromate and Prussian blue by leaching from the film during the intensification procedure. In this event it is necessary to omit the potassium bromide from the bleach bath and/or reduce the amount of potassium ferricyanide.

The high degree of intensification attainable through employment of this invention makes practicable the use of bipacks and tripacks hitherto handicapped by (1) halation from the front film support which could in the past be eliminated only by antihalation tints which reduce emulsion speed, (2) low resolution in rear films due to poor contact between front and rear films during exposure, and (3) low photographic speed.

For certain applications of photography it is sometimes desirable to place one film in front of another without appreciably decreasing the intensity and resolution of the light image recording in the rear film. For example, bipack photography has been used in color photography and also can be used in methods for forming silhouette masks for use in combining background and foreground scenes of different origin.

If a film as low in silver halide coating weight as that of Example I, or even lower, is used as a front film of an extended bipack film (such as the stripping rear film disclosed in Example I of Umberger U. S. application Ser. No. 274,287, filed February 29, 1952) there is little loss in sharpness and speed in the rear film. For color work, one can obtain separation negatives of surprisingly good quality by using a tripack composed of a very low coating weight blue record film in front of a bipack of green and red record films held in emulsion-to-emulsion contact. The base thickness interposed between the blue record emulsion and the contact point of the green and red record emulsions would normally seriously affect the image quality of the latter records. With approximately 5 mg. of silver halide per square decimeter in the front blue record film, however, adequate image quality is obtained in the green and red records. Following processing, the front film is intensified as described above and in Example I.

Another use of the procedure of this invention is the intensification of radiographs.

The invention can be used for the intensification of images in various types of photographic films including the negative extended bipack films of Jennings U. S. Patent 2,462,503, the stripping films of Marasco U. S. Patent 2,182,814, Rackett U. S. Patent 2,415,442, and Schule U. S. Patent 2,448,552, and the front film of bipacks exposed in beam-splitting cameras such as described on p. 753 in Neblette "Photography Principles and Practice," 4th ed., Van Nostrand (1942). The films of these references contain various natural and synthetic water-permeable colloids e. g. gelatin as binding agents in the image bearing layers.

The stripping and transfer operations can be carried out on any of the conventional apparatus used for registration and image transfer, e. g., the apparatus described in the following U. S. patents: Wyckoff et al. 1,303,836 and 1,303,837, Ball 1,661,157, Thornton 1,930,291, Whitney 1,707,699, Comstock 1,707,710, Rackett 2,271,572, Rackett 2,369,176 and 2,415,442, Capstaff 2,417,060 and Conklin 2,578,514.

The various advantages of this invention reside in the fact that controllable increases, up to ten-fold, in the density or contrast are obtained. Another advantage is that readily available materials are used. A further advantage is that intensified images which are stable and of good color can be obtained.

Another advantage of the invention is that it becomes possible to obtain normal speed and gamma (about 0.8) from silver halide coating weights as low as 5 to 10 mg. per square decimeter. With coating weight as low as this in the blue record or color camera negative films, very high speed and resolution result in the underlying green and red record emulsion layers.

Grain size is increased by the intensification process of this invention but probably the "grain" is diffused during printing. Thus, when printing the toned negative with blue light, the lead chromate grains absorb the light. The Prussian blue grains are essentially colorless to blue light and scatter or diffuse the "grainy" pattern produced by the lead chromate particles.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A process for intensifying a silver photographic image which comprises treating a photographic element bearing a silver image in a water-permeable layer thereof, in an aqueous solution containing ferricyanide ions in an amount corresponding to 0.5 to 25.0 grams per liter of a soluble ferricyanide compound and at least one cation which forms relatively insoluble ferrocyanide and chromate compounds in an amount equivalent to 1.0 to 25.0 grams per liter of lead nitrate and treating the resulting relatively insoluble ferrocyanide salt image in an aqueous solution containing at least one polyvalent metal cation which forms a relatively water-insoluble ferrocyanide compound in an amount equivalent to 0.01 to 0.1 molar concentration of ferric salt and at least one blue-light-absorbing complex oxide anion of hexavalent chromium in an amount equivalent to 0.5 to 25.0 grams per liter of sodium chromate.

2. A process for intensifying silver photographic images which comprises treating a photographic element bearing a silver image in a water-permeable layer thereof, in an aqueous solution containing ferricyanide ions in an amount corresponding to 0.5 to 25.0 grams per liter of a soluble ferricyanide compound and at least one cation taken from the group consisting of lead, zinc, silver, mercury, copper, nickel, cobalt, and cadmium ions until said silver image is converted to a metal ferrocyanide image of the latter metals, said cation being present in an amount equivalent to 1.0 to 25.0 grams per liter of lead nitrate, and treating the resulting element in an aqueous solution containing at least one polyvalent metal cation which forms

a relatively water-insoluble ferrocyanide compound in an amount equivalent to 0.01 to 0.1 molar concentration of ferric salt and at least one blue-light-absorbing complex oxide anion of hexavalent chromium in an amount equivalent to 0.5 to 25.0 grams per liter of sodium chromate.

3. A process for intensifying silver photographic images which comprises treating a photographic element bearing a silver image in a water-permeable layer thereof, in an aqueous solution containing ferricyanide ions in an amount corresponding to 0.5 to 25.0 grams per liter of a soluble ferricyanide compound and lead cations in an amount equivalent to 1.0 to 25.0 grams per liter of lead nitrate, until the silver image is converted to a lead ferrocyanide image, and treating the resulting element in an aqueous solution containing at least one polyvalent metal cation which forms a relatively water-insoluble ferrocyanide compound in an amount equivalent to 0.01 to 0.1 molar concentration of ferric salt and at least one blue-light-absorbing complex oxide anion of hexavalent chromium in an amount equivalent to 0.5 to 25.0 grams per liter of sodium chromate.

4. A process for intensifying silver photographic images which comprises treating a photographic element bearing a silver image in a water-permeable layer thereof, in an aqueous solution containing ferricyanide ions in an amount corresponding to 0.5 to 25.0 grams per liter of a soluble ferricyanide compound and lead cations in an amount equivalent to 1.0 to 25.0 grams per liter of lead nitrate, until the silver image is converted to a lead ferrocyanide image, and treating the resulting element in an aqueous solution containing a soluble ferric salt which forms a relatively water-insoluble ferrocyanide compound in an amount equivalent to 0.01 to 0.1 molar concentration of ferric salt and an alkali-metal dichromate in an amount of 0.5 to 25.0 grams per liter.

5. A process as set forth in claim 4 wherein the lead salt is lead nitrate and the ferric salt is ferric nitrate.

6. A process for intensifying silver photographic images which comprises treating a photographic element bearing a silver image in a water-permeable layer thereof, in an aqueous solution containing ferricyanide ions in an amount corresponding to 0.5 to 25.0 grams per liter of a soluble ferricyanide compound and lead cations in an amount equivalent to 1.0 to 25.0 grams per liter of lead nitrate, until the silver image is converted to a lead ferrocyanide image, and treating the resulting element in an aqueous solution containing a soluble ferric salt which forms a relatively water-insoluble ferrocyanide compound in an amount equivalent to 0.01 to 0.1 molar concentration of ferric salt and an alkali metal chromate in an amount of 0.5 to 25.0 grams per liter.

7. A process for intensifying silver photographic images which comprises treating the photographic film element bearing a silver image in a water-permeable colloid layer thereof, in an aqueous solution containing acetic acid, lead nitrate in an amount of 1.0 to 25.0 grams per liter, potassium ferricyanide in an amount of 0.5 to 25.0 grams per liter and potassium bromide in an amount of 1.0 to 25.0 grams per liter until the silver image is converted to a lead ferrocyanide image, and treating the resulting film element in an aqueous solution containing fer-

ric nitrate in 0.01 to 0.1 molar concentration of ferric salt, potassium dichromate in an amount of 0.5 to 25.0 grams per liter and potassium ferricyanide in an amount of 0.5 to 25.0 grams per liter.

5 8. A process for intensifying silver photographic images which comprises treating the photographic film element bearing a silver image in a water-permeable colloid layer of a said photographic element, in an aqueous solution containing acetic acid, lead nitrate in an amount of 1.0 to 25.0 grams per liter, potassium ferri-
 10 cyanide in an amount of 0.5 to 25.0 grams per liter and potassium bromide in an amount of 1.0 to 25.0 grams per liter until the silver image
 15 is converted substantially completely to a lead ferrocyanide image, and treating the resulting film element in an aqueous solution containing ferric nitrate in an amount of 0.01 to 0.1 molar
 20 concentration of ferric salt, potassium chromate

in an amount of 0.5 to 25.0 grams per liter and potassium ferricyanide in an amount of 0.5 to 25.0 grams per liter.

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