

1

3,140,177 PROCESSING COLOR PHOTOGRAPHIC MATERIALS

Maurice E. Welch, Brockport, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey
No Drawing. Filed Nov. 10, 1960, Ser. No. 68,359
9 Claims. (Cl. 96—56)

This invention relates to color photography and particularly to a method for emulsion hardening and prevention of magenta-fading in color photographic materials.

In processes of photographic color development, it is frequently desirable to use a formaldehyde hardening bath for purposes of hardening the emulsion layers. As is well known, formaldehyde will act as an emulsion layer hardener when used in a treating bath of alkaline pH.

In processes of color development, there frequently results the formation of stain in the white image areas or fading in which the dye in the image areas becomes decolorized. In either case the problem may result from unused dye-forming coupler remaining in the emulsion layer after processing. Particularly subject to this difficulty has been the magenta-dye-forming emulsion layer resulting from unused magenta coupler remaining in the layer after processing.

It has now been found that by the use of a particular acid-aldehyde bath as a final treating bath, each of the aforementioned difficulties can be overcome which at the same time has the end function of hardening the emulsion layer. It was very unexpected to find that polycarboxylic acid-formaldehyde solutions would harden the emulsion layer since it is well known that formaldehyde to be effective as a hardener must be present in an alkaline solution. While it is true that formaldehyde must be in an alkaline solution to impart hardness while wet, I discovered that polycarboxylic acid-formaldehyde solutions would impart hardness to the emulsion layer, while at the same time preventing magenta stain and fading, if the emulsion layer was dried in the presence of the acid-aldehyde treating solution. Clearly, therefore, my invention comprises a specialized procedure for color photographic development employing a polycarboxylic acid-aldehyde treating bath.

The processes of photographic color development to which my invention pertains relates to processes which produce dyed images in emulsion layers where the color-forming couplers are incorporated directly in such layers. Processes of this type have been described in Fischer U.S. Patent 1,055,155, granted March 4, 1913.

It is an object of the present invention to provide a process whereby magenta-fading can be prevented in color coupler incorporated multilayer photographic materials. Another object is to provide a process whereby the emulsion layers can be hardened in the single step which also prevents magenta-fading. A further object is to provide a treating bath which can be employed in a process of this invention to accomplish the objects herein stated.

These objects are accomplished by a special procedure for processing of color coupler incorporated multilayer photographic materials, which employs as a final treatment a treating bath comprising a water-soluble polycarboxylic acid and an aliphatic aldehyde selected from the group consisting of formaldehyde, paraformaldehyde, and acetaldehyde. The water-soluble polycarboxylic acids which can be employed in this invention comprise polycarboxylic acids having from 2 to 6 carbon atoms. Suitable acids comprise oxalic, malonic, malic, tartaric, citric, succinic, glutaric and adipic. According to the invention the photographic material being processed is treated for a short time in a bath of the above composition after which the photographic material is dried with

2

no further treatment. The time of treatment with the treating bath can vary widely but from about 15 seconds to about 30 seconds is adequate. Drying of the material after treatment can be in any conventional manner.

The polycarboxylic acid-aldehyde treating bath of my invention can be used as the final treating bath after conventional color processing procedures. The bath does not form an insoluble complex and is not precipitated by reaction with residual developing agents, fixers, etc., which may be retained by the film or in the layers thereof. Likewise, no difficulty has been encountered with the operativeness of the processing equipment through the use of the bath. The bath is not unusually corrosive and sludge or other undesirable developments have not occurred where the present baths have been employed.

The colored photographic materials treated according to the invention comprise color materials where the couplers are incorporated in the sensitive emulsion layers. According to one embodiment of this invention, multilayer emulsion layers containing color formers or couplers, such as those described in U.S. Patent 2,322,027, issued June 15, 1943, are developed for approximately 2 minutes and 15 seconds in a developer of the following

composition:

Water	ml.	800
Benzyl alcohol	ml.	12.0
Calgon	g.	2.0
Sodium sulfite	g.	2.0
Sodium carbonate	g.	22.0
Sodium bicarbonate	g.	2.75
Sodium bromide	g.	0.4
Sodium chloride	g.	0.59
4 - amino - N-ethyl-N-(methanesulfonamidoethyl)-m-toluidinesulfate monohydrate	g.	4.0
Water to make 1 liter.		

After development, the print material is washed for about 5 seconds with a fine spray and shortstopped in an acid stop bath, such as

Water	ml.	800
Acetic acid (glacial)	ml.	8.6
Water to make 1 liter.		

The print material is then bleached in a ferricyanide bleach, such as follows:

Water	ml.	800
Borax	g.	1
Sodium ferrocyanide, decahydrate	g.	25.7
Potassium persulfate	g.	6.1
Sodium bromide	g.	4.75
Boric acid	g.	13.3
Sodium nitrate	g.	30.0
Water to make 1 liter.		

After a short rinse, the color print material is then fixed in a hypo fixing bath, such as

Water	ml.	800
Sodium thiosulfate	g.	150
Sodium sulfite	g.	15
Acetic acid (glacial)	ml.	12
Zinc sulfate monohydrate	g.	8
Borax	g.	3.1

Water to make 1 liter.

After fixing, multicolor print material was briefly washed and treated for approximately 15 to 30 seconds in a polycarboxylic acid-aldehyde treating bath as set forth in the following examples and then dried with no further treatment.

The following examples illustrate final treating baths according to my invention:

3

EXAMPLE 1

Borax -----g-- 20.8
 Citric acid-----g-- 36.6
 Formaldehyde -----ml-- 3.75
 Water to make 1 liter.
 Final pH of the bath was pH 3.5.

EXAMPLE 2

Sodium metaborate-----g-- 18
 Citric acid-----g-- 30
 Formalin (37.5 percent formaldehyde)-----ml-- 10
 Water to 1 liter.
 Final pH of the bath was pH 3.6.

EXAMPLE 3

Borax -----g-- 20.8
 Tartaric acid-----g-- 18.1
 Formaldehyde -----ml-- 5.0
 Water to 1 liter.
 Final pH of the bath was pH 3.5.

EXAMPLE 4

Borax -----g-- 4.3
 Succinic acid-----g-- 20.0
 Formalin (37.5 percent formaldehyde)-----ml-- 15.0
 Water to 1 liter.
 Final pH of the bath was pH 3.5.

EXAMPLE 5

Borax -----g-- 5.1
 Succinic acid-----g-- 20.0
 Acetaldehyde -----g-- 22.0
 Water to 1 liter.
 Final pH of the bath was pH 3.5.

After a short rinse in any one of the final treating baths of the above compositions and after drying with no further treatment, there was obtained a multicolor print containing stain-free, positive dye images of excellent brilliance and freedom from color degradation. The prints produced by the novel procedure of this invention resulted in multicolor prints which were not subject to magenta dye-fading in the image areas. The prints were also stable against the formation of a yellow stain in the high light or white areas of the prints.

Where the final treating bath of my invention was used according to the procedure herein described, the processed prints were stable against magenta-fading throughout a ten-day test period in a dry oven at 140° F. and 20 percent relative humidity, whereas comparable prints processed in a conventional manner lost 0.2 density unit in a magenta patch having a green density of 1.0.

In the polycarboxylic acid-aldehyde treating baths of my invention, the pH of the bath for optimum results can advantageously be within the range of about pH 3.0 to about pH 4.0. The most useful range is from about pH 3.3 to about pH 3.7. In preparing the bath, a compound which has a buffering action with the polycarboxylic acid is normally used; one such buffering compound is borax. The useful range of concentration for the polycarboxylic acid can vary widely. Ordinarily the polycarboxylic acid compound is added in the treating bath in the amount from about 0.5 percent to about 15.0 percent. Where the higher amounts of polycarboxylic acid are used, as is apparent, a correspondingly greater amount of a buffering compound would be needed to give desired pH.

An aldehyde of this invention can be added to the treating bath in an amount which can vary over a wide range. A useful concentration in the bath is from about 0.1 percent to about 10 percent, with the most useful concentration in the range from about 1 percent to about 4 percent.

The treating bath, when used as a final bath in the processing sequence, produces (1) an improved magenta

4

dye stability and (2) hardening of the gelatino-emulsion layer. Improved dye stability is thought to occur in that the bath functions to tie up unused coupler so that it does not react with magenta dye to produce a colorless product. Particularly in low density areas, large amounts of unused coupler remain since only a small amount of coupler has been used to form the magenta dye image. The colorless effect produced is commonly referred to as fading and more specifically as pink toe fade.

The hardening effect which is obtained according to the present invention can be obtained in photographic materials other than those which are subject to magenta fading as indicated above. It will be apparent that the hardening effect obtained through the use of the treating baths of this invention, when used as a final treatment, can be obtained in any of the gelatino-type photographic emulsions.

Color print materials prepared according to the disclosure in U.S. Patent 1,055,155, referred to above, which had been processed according to the procedure of this invention and which employed the final treating bath, were checked for degree of hardness imparted by the invention. To make this determination, three strips of the processed print material were placed in a beaker of water at room temperature. The temperature of the water was then raised to boiling, which took about 35 minutes, and then continued at boiling for a total time of about 65 minutes. The results of the determination are given in the following example.

EXAMPLE 6

The three strips of processed color material were given a final treatment in a treating bath having a composition as given below. After final treatment, each strip was dried at room temperature overnight.

Basic Composition for Final Treating Bath

Borax -----g-- 25.0
 Adipic acid-----g-- 40.0
 Water to make 1 liter (final volume).
 Final pH of the bath was pH 3.6.

Final Treating Bath	Reticulation Time	Melting Time
Strip 1—No formalin in final treating bath.	35 minutes....	35 minutes.
Strip 2—10 ml. formalin per liter in final treating bath.	40 minutes....	42 minutes.
Strip 3—40 ml. formalin per liter in final treating bath.	None after 60 minutes.	None after 60 minutes.

The results of this example show that a degree of hardness is imparted to the emulsion layers where the polycarboxylic acid-aldehyde final bath is employed without subsequent washing.

In accordance with the present invention, the magenta dye step images are produced by color-developing silver halide emulsions containing magenta color formers with a suitable aromatic primary amino color developing agent. Suitable developing agents comprise 4-aminoaniline, 4-ethylaminoaniline, 2-diethylaminoaniline, 4-dialkylaminoaniline, e.g., 4-dimethylaminoaniline, 4-diethylaminoaniline, 4-[N-(β -hydroxyethyl)-N-ethyl]-aminoaniline, 4-amino-N-ethyl-N-(β -methanesulfonamidoethyl)-2-methylaniline sulfate, and the like. These developing agents are preferably used in the form of their salts, such as the hydrochloride or hydrosulfate, since in this form they are more soluble and stable than the free bases. Other suitable color developers have been described in U.S. Patents 2,213,986, issued September 10, 1940, and 2,902,366, issued September 1, 1959. The oxidation products of any of these aromatic primary amino developing agents couple with the pyrazolone color former to form a magenta dye image of the azomethine type in the emulsion. After removal of the silver image by bleaching and fixing in a manner well known in the art, the

color image remains in the emulsion and it is to the preservation of this magenta image to which the present invention pertains.

A procedure for the process of forming colored images in photographic color materials is fully described in U.S. Patent 2,486,440, issued November 1, 1949.

Typical couplers, which form the magenta image in multicolor photographic materials, are pyrazolone compounds. Examples of such pyrazolone compounds are the following:

1-phenyl-3-(4'- α -sulfosteamido)-phenoxyacetamido-5-pyrazolone
 1-phenyl-3-(4'- α -sulfosteamido)-phenylacetamido-5-pyrazolone
 1-phenyl-3-(4'- α -sulfosteamido)-benzamido-5-pyrazolone
 1-phenyl-3-(3'- α -sulfosteamido)-benzamido-5-pyrazolone
 1-phenyl-3-methyl-4-paradimethylaminobenzal-5-pyrazolone
 1-phenyl-3-methyl-4-phenylmethylmethylene-5-pyrazolone
 1-phenyl-3-methyl-4-phenylethylidene-5-pyrazolone
 1-phenyl-3-methyl-4-m-nitrophenylmethylmethylene-5-pyrazolone
 3-N-acetylaniline-5-pyrazolone
 1-phenyl-3-hydroxy-5-phenyliminopyrazolone

The pyrazolone compounds indicated herein can be prepared according to the disclosures of U.S. Patents 2,213,986; 2,902,366; and 2,311,081 and 2,311,082, issued February 16, 1943.

The present development process can be employed for the production of colored photographic images in layers of gelatin which are supported by a transparent medium such as glass, a cellulose ester, or an opaque reflecting medium such as paper. The emulsion can be coated as a single layer on the support or as superimposed layers on one or both sides of the support.

The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. In the preparation of a finished multicolor photographic element containing in a gelatin substrate a magenta image and a substantial amount of residual pyrazolone photographic color coupler capable of coupling with the oxidation products of an aromatic amino photographic color developer to form a magenta image, the process which comprises treating as a final processing step said photographic element with an aqueous treating bath comprising

(1) 0.1% to 10% of an aldehyde selected from the class consisting of formaldehyde and acetaldehyde, and

(2) 0.5% to 15% of a water-soluble polycarboxylic acid having 2 to 6 carbon atoms, said treating bath having a pH of about 3 to 4, and thereby hardening said gelatin and reducing fading of said magenta image.

2. The process of claim 1 wherein the treating bath comprises a solution of formaldehyde and a water-soluble polycarboxylic acid containing from 2 to 6 carbon atoms.

3. The process of claim 1 wherein the treating bath comprises a solution of formaldehyde and citric acid.

4. The process of claim 1 wherein the treating bath comprises a solution of formaldehyde and tartaric acid.

5. The process of claim 1 wherein the treating bath comprises a solution of formaldehyde and succinic acid.

6. The process of claim 1 wherein the treating bath comprises a solution of acetaldehyde and succinic acid.

7. The process of claim 1 wherein the treating bath comprises a solution of formaldehyde and adipic acid.

8. In the preparation of a finished multicolor photographic element containing in a gelatin substrate a magenta image and a substantial amount of residual pyrazolone photographic color coupler capable of coupling with the oxidation products of an aromatic amino photographic color developer to form a magenta image, the process which comprises treating as a final processing step said photographic element with an aqueous treating bath comprising

(1) 1% to 4% of an aldehyde selected from the class consisting of formaldehyde and acetaldehyde, and

(2) 0.5% to 15% of a water-soluble polycarboxylic acid selected from the class consisting of citric acid, tartaric acid, succinic acid, and adipic acid,

said treating bath having a pH of about 3 to 4, and thereby hardening said gelatin and reducing fading of said magenta image.

9. The process of claim 8 wherein borax is used in the treating bath as a buffer to maintain the pH of the treating bath at a pH of 3 to 4.

References Cited in the file of this patent

UNITED STATES PATENTS

45	2,518,686	Harsh et al. -----	Aug. 15, 1950
	2,579,435	Mackey -----	Dec. 18, 1951
	2,579,436	Mackey -----	Dec. 18, 1951
	2,657,139	Bates -----	Oct. 27, 1953
50	2,788,274	Ranger -----	Apr. 9, 1957
	2,913,338	Bates et al. -----	Nov. 17, 1959
	3,095,302	Jeffreys et al. -----	June 25, 1963

OTHER REFERENCES

55	Royals: "Advanced Organic Chemistry," Prentice-Hall, N.J., January 1956, page 780 relied upon.
----	--