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3,473,929

METHOD OF INHIBITING DISCOLORATION OF COLOR PHOTOGRAPHS

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No Drawing. Filed Sept. 9, 1965, Ser. No. 486,236
Int. Cl. G03c 7/30

U.S. Cl. 96—56

7 Claims

ABSTRACT OF THE DISCLOSURE

The discoloration of completely processed color photographs caused by prolonged exposure to light, elevated temperatures and elevated humidity is advantageously inhibited by imbibing in said photograph an aqueous solution of a stabilizing compound having at least one tri(hydroxymethyl)-methyl group and then drying said photograph while it still contains a substantial quantity of said stabilizing compound.

This invention relates to color photography and more particularly to methods for preventing discoloration of photographic layers containing dye images.

The images of color photographs produced by many photographic processes, for example those processes involving the color development of imagewise exposed photographic silver halide emulsion layers, comprise dyes which are present in water permeable layers carried by a support such as paper or film base. These dyes are, in general, not highly stable, and so color photographs tend to be discolored if exposed to bright light, particularly direct sunlight, or stored under adverse temperature and humidity conditions for long periods. Discoloration can be due both to differences between the fading rates of the dyes, usually cyan, magenta and yellow dyes, in the image, and to the formation of an overall stain from chemicals in the image-containing layers, or elsewhere. Such a stain is sometimes termed "print-out."

In photographic processes involving color development, the couplers may be in the color developer solutions or may be incorporated in the emulsion layers. Examples of couplers which may be used in developer solutions are given in "The Theory of the Photographic Process" by C. E. K. Mees (revised edition, 1954) on pages 588-589; examples of couplers which may be incorporated in emulsion layers are given on pages 598-599. Dyes produced by color development are, in general, indoaniline, azomethine, indophenol and indamine dyes.

Materials for the production of color photographs by processes involving color development are described on pages 305-307 of "Principles of Color Photography," Evans, Hanson and Brewer (New York, 1953), and include the materials well known under the registered trademarks "Kodachrome," "Kodacolor," "Ektachrome" and "Ektacolor."

Many indophenol, indamine, indoaniline and azomethine dyes are relatively unstable to light with the result that dye images in finished commercial color pictures have a tendency to fade, especially when subjected to intense illumination for extended periods of time. This is true whether the source of illumination is sunlight or tungsten or fluorescent lamps. The cyan dyes are generally relatively less susceptible to fading than the other dyes commonly used in color photography. In processes in which the couplers are incorporated in the emulsion layers or in plain gelatin layers in the film, further difficulty is caused by residual unused couplers which tends to print-

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out as a stain, usually a yellow stain, under the influence of light, especially in the highlight areas of the picture. Magenta dye-forming couplers are generally more susceptible to print-out than others.

One solution to the problem of fading of dye images and print-out of residual couplers in photographic layers would be to use only couplers and dyes which are inherently stable to light. This is seldom feasible, however, since the number of couplers and dyes suitable for use in commercial photographic color processes is somewhat limited and it is often the case that the most suitable materials are not as stable as might be desired. Therefore, the most satisfactory approach to the fading and print-out problem has been to choose couplers and dyes suitable for the particular photographic process and then attempt to protect these compounds against the usually deleterious effects of light.

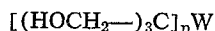
In general, two methods have been suggested to prevent the discoloration of photographic layers. One of these comprises overcoating the photographic layer to be protected with an ultraviolet light absorbing material. Methods of this type are disclosed in Salminen et al., U.S. Patent 2,632,701 issued Mar. 24, 1953, and Edgerton et al., U.S. Patent 2,747,996 issued May 29, 1956. The other method referred to comprises treatment of photographic layers containing dye images with certain chemical compounds, particularly organic reducing agents or antioxidants, in order to stabilize the dye images and any residual coupler in the photographic layers. Methods of this type are disclosed in Vittum, U.S. Patent 2,384,658 issued Sept. 11, 1955 and Mackey, U.S. Patent 2,579,435 issued Dec. 18, 1951. Methods of the latter type have been found to be entirely empirical. For example, although the reducing agents of the Vittum patent are useful, others of similar reducing properties have no effect on the stability of photographic dye images. Further, many reducing compounds which might suggest themselves as stabilizing agents not only have no stabilizing properties but actually cause stain or destruction of dye images in photographic layers. It has, therefore, been difficult to find compounds having appreciable dye stabilizing or anti-print-out properties which are also free from other undesirable characteristics. Therefore, although the above and other methods have been suggested in the art for protecting colored photographic elements against discoloration due to fading or print-out, none has proven to be a complete solution to the problem and the search for new methods has continued.

It is an object of the present invention to provide a method for preventing dye fading and print-out in processed color photographs comprising treating the said processed material with certain compounds containing at least one trimethylol methyl group. It is a further object of the invention to provide color photographic materials including films, transparencies and prints stabilized against discoloration under the influence of prolonged exposure to light, elevated temperatures and high humidities. Other objects will be apparent from the following description of the invention.

According to our invention these and other objects are accomplished by contacting the dye image containing a completely processed color photograph that is substantially free from developed silver, silver halide and soluble salts, with an aqueous solution containing a stabilizing compound having at least one tri(hydroxymethyl)methyl group. The photographic element is allowed to remain in contact with the said solution until said element is impregnated with the said stabilizing compound, and then the said element is dried while it still contains a substantial quantity of the said compound.

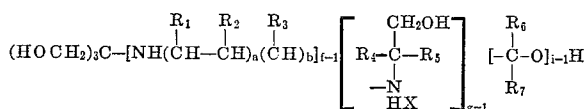
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Our polymethylol stabilizing compounds are advantageously represented by the formula:



in which n is an integer of from 1 to 2; and W represents a member selected from the class consisting of carboxy and an amino group.

Our stabilizing compounds include those represented by the formula:



wherein a and b , each represents an integer of from 0 to 1; f , g and i each represents an integer of from 1 to 2; R_1 , R_2 and R_3 each represents hydrogen or hydroxyl; R_4 and R_5 each represents hydrogen or hydroxymethyl; R_6 and R_7 each represents hydrogen or together represent an oxygen atom; and the salts formed by adding HX wherein X represents an acid anion (e.g., chloride, bromide, iodide, perchlorate, sulfate, acetate, propionate, citrate, etc.) to one or both nitrogen atoms in the above formula.

Typical stabilizing compounds used to illustrate our invention include the following:

- (1) 3-hydroxy-2,2-dihydroxymethyl-propionic acid
- (2) 2-amino-2-hydroxymethylpropane-1,3-diol
- (3) 2,2,8,8-tetrahydroxymethyl-3,7-diazanonane-1,5,9'-triol dihydrochloride
- (4) 3,2'-hydroxyethyl-8,8-dihydroxymethyl-3,7-diazanonane-1,5,9-triol dihydrochloride
- (5) 2,2-dihydroxymethyl-3-azapentane-1,5-diol hydrochloride

Compound 2 is sometimes known as "tris-buffer." Compounds 3 to 5 are derivatives of compound 2 and can be prepared by the method of Pierce and Wotis, J. American Chemical Soc., 66, 880 (1944). Many of our compounds are available. Those that aren't are readily prepared by the methods described in the said reference, U.S. Patent 2,408,096, etc.

Although our stabilizing compounds are used to advantage in aqueous solutions over a wide range of concentrations, it is preferred that the concentration be at least 2.5% by weight, and a concentration of approximately 10% by weight often being particularly suitable. It is also preferred that the solution be neutral or acidic, because in some cases the use of an alkaline solution may result in the formation of yellow "print-out" when the treated photograph is exposed to large amounts of light. When it is necessary to neutralize or acidify the solution, a mineral acid, such as hydrochloric acid, or an organic acid such as citric acid can be used.

The aqueous solution of our invention may contain additional solutes including, for example, buffering agents, preservatives for inhibiting mold growth in the solution, and known stabilizing agents. Only solutes which are shown not to seriously interfere with the stabilization produced by our stabilizing compounds should be included in the solution.

The process of the invention can be carried out either during the processing procedure used for the production of a color photograph, before the latter has been dried, or afterwards.

In some cases it may be possible to modify a processing procedure so as to comprise a process of the invention simply by including a polymethylol compound in the solution last used in the procedure.

In carrying out the process of the invention, it is often convenient to immerse the photograph completely in the stabilizing solution, but it is sometimes preferable to apply the solution only to the image side which can be done by spraying, for example. The solution should be left in contact with the image side of the photograph for a few minutes (a time of from 5 to 10 minutes

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is generally adequate) to allow the image-containing water-permeable layers to be impregnated with the polymethylol compound. It is generally satisfactory and convenient to carry out the treatment at room temperature.

It is usually desirable to remove surplus stabilizing solution from a treated color photograph before drying. This can be done by squeegeeing. If more thorough removal of surplus solution is needed, as can be the case when the color photograph has a non-absorbent support such as film base, the photograph can be momentarily rinsed, but care must be taken to leave enough of the polymethylol compound in the photograph to stabilize the image.

Our invention is still further illustrated by means of the following typical examples.

Example 1

Two identical sets of color processed multilayer multi-color reversal film with cyan, magenta and yellow dye images were prepared. The films were substantially free of silver, silver halide and soluble salts. One set was treated for 10 minutes in an aqueous solution containing 9% of stabilizing compound No. 1 buffered to a pH of 7 with sodium hydroxide solution. The treated transparencies were squeegeed and allowed to dry. The other set was treated with water for 10 minutes and then dried. One-half of each set of transparencies was held as a control while the other half of each set was exposed for two weeks to light from a 500-watt tungsten lamp at a distance of 8½ inches. The transparencies were stored at about 25° C. A comparison of the exposed transparencies with the controls showed that there was a considerable improvement in magenta and yellow dye stabilities in the transparencies treated with the stabilizing compound 1 solution.

Example 2

Example 1 was repeated using a 10% aqueous solution of stabilizing compound No. 2 that was adjusted to a pH of 7.0 with hydrochloric acid. The magenta and yellow image dye stabilities to prolonged exposures to the tungsten lamp were substantially improved as a result of the stabilizing treatment.

Example 3

Example 2 was repeated using a 10% aqueous solution of stabilizing compound No. 3. Substantial improvements were made in the stability of the magenta and yellow image dyes to prolonged exposure to tungsten illumination.

Example 4

Example 2 was repeated using a 10% solution of stabilizing compound No. 4. Substantial improvements were made in the stability of the magenta and yellow image dyes to prolonged exposure to tungsten illumination.

Example 5

Example 2 was repeated using a 10% solution of stabilizing compound No. 5. As in the preceding examples, the light stability of the magenta and yellow image dyes were substantially increased by the stabilizing treatment.

Example 6

Examples 1 and 2 were repeated using another multilayer, multicolor commercial reversal film product and a reversal color print material. In each case substantial improvement was produced in the stability of the magenta and yellow dye images to prolonged exposure to tungsten light.

Example 7

Three different multilayer multicolor print materials A, B and C containing different magenta and different yellow dye-forming couplers were exposed to a color image and given complete color processing. One-half of the processed samples were treated for 10 minutes at 70°

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F. in an aqueous solution containing 10% by weight of stabilizing compound No. 2 which had been adjusted to a pH of 7.0 with hydrochloric acid. After treatment, the prints were dried.

Samples of the processed color prints were subjected to the following conditions:

(1) South window for 28 days, 1,800,000 foot-candle hours.

(2) North window for 28 days, 520,000 foot-candle hours.

(3) Xenon arc Fadeometer, 117½ hours, 400,000 foot-candle hours.

The following tables summarize the results.

SOUTH WINDOW FADING

Stabilizing Bath Treatment		Percentage Dye Density Loss From an Initial Density of 1.0		
		Cyan	Magenta	Yellow
Color Print Material:				
A.....	None.....	10	86	29
A.....	Compound No. 2.....	14	32	22
B.....	None.....	9	41	94
B.....	Compound No. 2.....	5	32	70
C.....	None.....	16	98	38
C.....	Compound No. 2.....	19	53	38

NORTH WINDOW FADING

Stabilizing Bath Treatment		Percentage Dye Density Loss From an Initial Density of 1.0		
		Cyan	Magenta	Yellow
Color Print Material:				
A.....	None.....	10	40	19
A.....	Compound No. 2.....	14	18	17
B.....	None.....	8	23	73
B.....	Compound No. 2.....	11	19	41
C.....	None.....	15	96	26
C.....	Compound No. 2.....	15	39	32

FADEOMETER

Stabilizing Bath Treatment		Percentage Dye Density Loss From an Initial Density of 1.0			Stain Change		
		Cyan	Magenta	Yellow	Cyan	Magenta	Yellow
A.....	None.....	12	23	18	-.01	-.02	-.01
A.....	Compound No. 2.....	14	18	10	-.01	-.01	-.01
B.....	None.....	6	14	55	-.01	-.02	+.05
B.....	Compound No. 2.....	11	19	18	-.01	-.01	+.01
C.....	None.....	13	44	28	-.01	0	+.14
C.....	Compound No. 2.....	20	34	21	-.01	-.01	-.01

The data show that the percent loss in magenta dye in color prints from prolonged exposure to north window light was reduced from as high as 96% to 39% and that the percent loss in magenta dye in color prints from prolonged exposure to south window light was reduced from as high as 86% to 32% by treatment with an aqueous solution of stabilizing compound No. 2.

The data show that the percent loss in yellow dye in color prints from prolonged exposure to light from a north window was reduced from as high as 73% to 41% and from prolonged exposure to a xenon arc Fadeometer was reduced from as high as 55% to 18% by treatment with an aqueous solution of stabilizing compound No. 2.

The cyan dye density loss was generally small compared to the loss in magenta and yellow in untreated color prints.

Improvements in yellow stain in color prints given prolonged exposure in the Fadeometer were as high as from an increase in yellow stain of +.14 to a reduction of -.01 as a result of treatment with our solution of stabilizing compound No. 2.

Similar reductions in the discoloration of processed

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color photographs caused by prolonged exposure to light may be shown when still other stabilizing solutions of our invention are used to treat the completely processed color photograph prior to the light exposure.

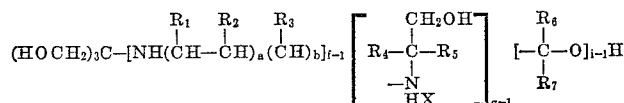
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as defined hereinabove and as described in the appended claims.

We claim:

1. The method of inhibiting the discoloration of com-

pletely processed color photographs caused by prolonged exposure to light, elevated temperature and elevated humidity, said photograph being substantially free of silver, silver halide and soluble salts, said method comprising the steps of:

(1) imbibing in said photograph an aqueous solution of a compound having the formula:



wherein *a* and *b* each represent an integer of from 0 to 1; *f*, *g* and *i* each represent an integer of from 1 to 2 such that at least one of *f*, *g* and *i* represents the integer 2; *R*₁, *R*₂ and *R*₃ each represents a member selected from the class consisting of hydrogen and hydroxyl; *R*₄ and *R*₅ each represent a member selected from the class consisting of hydrogen and hydroxymethyl; *R*₆ and *R*₇ each represent a member selected from the class consisting of hydrogen and when taken together an oxygen atom; and X represents an acid anion and

(2) allowing said photograph to dry containing sufficient absorbed compound to inhibit said discoloration of said photograph.

2. The method of inhibiting the discoloration of com-

pletely processed color photographs caused by prolonged exposure to light, elevated temperatures and elevated humidities, said photographs being substantially free of silver, silver halide and soluble salts, said method comprising the steps of:

- (1) imbibing in said photograph an aqueous solution of a compound selected from the class consisting of:

3-hydroxy-2,2-dihydroxymethylpropionic acid,
2-amino-2-hydroxymethylpropane-1,3-diol,
2,2,8,8-tetrahydromethyl - 3,7 - diazanonane - 1,5,9-
triol dihydrochloride,
3,2' - hydroxyethyl - 8,8 - dihydroxymethyl - 3,7-
diazanone-1,5,9-triol dihydrochloride, and
2,2 - dihydroxymethyl - 2- azapentane - 1,5 - diol
hydrochloride,

- (2) allowing said photograph to dry containing sufficient absorbed compound to inhibit said discoloration of said photograph.

3. The method of inhibiting the discoloration of completely processed color photographs caused by prolonged exposure to light, elevated temperatures and elevated humidities, said photographs being substantially free of silver, silver halide and soluble salts, said method comprising the steps of:

- (1) imbibing in said photograph an aqueous solution of a compound 3 - hydroxy - 2,2 - dihydroxymethylpropionic acid,

- (2) allowing said photograph to dry containing sufficient absorbed compound to inhibit said discoloration of said photograph.

4. The method of inhibiting the discoloration of completely processed color photographs caused by prolonged exposure to light, elevated temperatures and elevated humidities, said photographs being substantially free of silver, silver halide and soluble salts, said method comprising the steps of:

- (1) imbibing in said photograph an aqueous solution of a compound 2-amino-2-hydroxymethylpropane-1,3-diol,

- (2) allowing said photograph to dry containing sufficient absorbed compound to inhibit said discoloration of said photograph.

5. The method of inhibiting the discoloration of completely processed color photographs caused by prolonged

exposure to light, elevated temperatures and elevated humidities, said photographs being substantially free of silver, silver halide and soluble salts, said method comprising the steps of:

- (1) imbibing in said photograph an aqueous solution of a compound 2,2,8,8 - tetrahydromethyl - 3,7 - diazanonane-1,5,9-triol dihydrochloride,

- (2) allowing said photograph to dry containing sufficient absorbed compound to inhibit said discoloration of said photograph.

6. The method of inhibiting the discoloration of completely processed color photographs caused by prolonged exposure to light, elevated temperatures and elevated humidities, said photographs being substantially free of silver, silver halide and soluble salts, said method comprising the steps of:

- (1) imbibing in said photograph an aqueous solution of a compound 3,2'-hydroxyethyl - 8,8 - dihydroxymethyl-3,7-diazanone-1,5,9-triol dihydrochloride.

- (2) allowing said photograph to dry containing sufficient absorbed compound to inhibit said discoloration of said photograph.

7. The method of inhibiting the discoloration of completely processed color photographs caused by prolonged exposure to light, elevated temperatures and elevated humidities, said photographs being substantially free of silver, silver halide and soluble salts, said method comprising the steps of:

- (1) imbibing in said photograph an aqueous solution of a compound 2,2-dihydroxymethyl - 3 - azapentane-1,5-diol hydrochloride,

- (2) allowing said photograph to dry containing sufficient absorbed compound to inhibit said discoloration of said photograph.

References Cited

UNITED STATES PATENTS

2,384,663	9/1945	Weissberger et al.	96—56
2,487,569	11/1949	Mackey	96—56
3,095,302	6/1963	Jeffreys et al.	96—56
3,157,504	11/1964	Bard	96—56

J. TRAVIS BROWN, Primary Examiner

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,473,929 Dated 10/21/69

Inventor(s) Jeffreys and Williams

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 7, line 14, between dihydroxymethyl-" and "-azapentane", delete "2" and substitute in its place --3--.

SIGNED AND
CELED
JAN 5 1971

SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents