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3,069,262

PROCESSES FOR FORMING DYE DEVELOPER IMAGES HAVING STABILITY IN SUNLIGHT**Howard C. Haas, Arlington, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware****No Drawing. Filed Mar. 27, 1958, Ser. No. 724,249
20 Claims. (Cl. 96—29)**

The present invention relates to photography and more particularly to processes for protecting color diffusion transfer images from the deteriorating effects of sunlight.

One object of this invention is to provide colored diffusion transfer images having enhanced stability in sunlight, and also to provide processes for obtaining such improved stability.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

The copending U.S. application of Howard G. Rogers, Serial No. 415,073, filed March 9, 1954, now abandoned and replaced by application Serial No. 748,421, filed July 14, 1958, now U.S. Patent No. 2,983,606, issued May 9, 1961, discloses and claims processes wherein dye developers (i.e. dyes which contain, in the same molecule, a silver halide developing function and a chromophoric system of a dye) are used to form color transfer images. In such processes, a photosensitive element is exposed to create therein a latent image. The latent image is developed in the presence of a dye developer and an imagewise distribution of unreacted dye developer, from which the positive image may be created, is formed. At least a portion of said unreacted dye developer is transferred to a superposed image-receiving element to create thereon a positive image. The processes are preferably carried out by disposing the dye developer in the photosensitive element prior to exposure and causing it to be solubilized therefrom by an alkaline processing liquid which is applied between the superposed photosensitive element and image-receiving element. As the process proceeds, the exposed silver halide is reduced to metallic silver and the portions of the dye developer, which are oxidized as a result of the silver development, are substantially immobilized in exposed areas. At least a portion of the unreacted dye developer is imbibed on the superposed image-receiving element to create thereon the positive dye image. The positive image is preferably viewed by stripping the photosensitive element from the image-receiving element.

The color fastness of the colored photographic images, produced in such processes, upon prolonged exposure to sunlight often leaves something to be desired. I have discovered that by using a compound selected from the group consisting of pyrogallol, gallic acid and esters of gallic acid (i.e., esters wherein the acid group of the gallic acid is esterified with an alcohol) to protect the image, the color stability of the images in sunlight is appreciably enhanced.

One method of using the above-named stabilizers is to treat the finished colored image with a solution comprising the stabilizer to be used. The solution may conveniently be applied to the colored image by immersion, swabbing, coating, spraying, flowing, etc. In an especially

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useful embodiment, the solution may also comprise a film-forming polymer, such as gelatin, which will serve as a protective surface coating for the image. In addition, the solution may comprise other stabilizing agents such, for example, as ultraviolet absorbers, etc. Depending upon the solvents present in the solution containing the stabilizer, and upon whether a film-forming polymer is included, the stabilizer may be present in a layer over the image-receiving layer or it may, at least in part, permeate into the image-receiving layer.

Another mode of carrying out the processes of this invention is to incorporate the stabilizers herein disclosed into the image-receiving element prior to its use in the dye developer transfer processes. The image-receiving element, into which the stabilizer is incorporated, generally comprises a sheet of dye-receptive material and, in preferred embodiments, comprises a support bearing a coating of a dyeable material. The stabilizer may be incorporated by adding it to the coating solution of dyeable material and applying it therewith, or it may be applied, as above, by permeation. As examples of dyeable materials which have been found useful in preparing image-receiving elements, mention may be made of nylons such as Nylon Type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for N-methoxymethyl polyhexamethylene adipamide), polyvinyl alcohol, crosslinked polyvinyl alcohol (i.e., polyvinyl alcohol which has been reacted with a cross-linking agent such as glyoxal or dimethylolurea), mixtures of polyvinyl alcohol and poly-N-vinyl pyrrolidone, and copolymers of vinyl alcohol and N-vinyl pyrrolidone.

Still another mode of carrying out the processes of this invention is to incorporate the stabilizers herein disclosed into the image-receiving element both before its use in transfer processes and again after the positive image has been formed thereon. Such a mode is especially effective in assuring an intimate association of the stabilizers herein disclosed with the dye developers which they are intended to protect.

Dye developers, as noted above, are compounds which contain in the same molecule both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide developing function is a hydroquinonyl group. Other suitable developing functions include o-dihydroxyphenyl and o- and p-amino-substituted hydroxyphenyl groups. In general, the developing function includes a benzenoid developing function. Examples of representative dye developers are given in the previously mentioned application of Howard G. Rogers. Additional useful dye developers are described in the following copending U.S. applications:

Application Serial No. 449,514, filed August 12, 1954, in the names of Elkan R. Blout and Myron S. Simon, now abandoned and replaced by continuation-in-part application Serial No. 849,727, filed October 30, 1959.

Application Serial No. 450,208, filed August 16, 1954, in the names of Elkan R. Blout, Saul G. Cohen, Milton Green and Myron S. Simon, now abandoned and replaced by continuation-in-part application Serial No. 755,804, filed October 18, 1958.

Application Serial No. 471,542, filed November 26, 1954, in the names of Elkan R. Blout, Saul G. Cohen, Milton Green, Howard G. Rogers, Myron S. Simon and Robert B. Woodward, now abandoned and replaced by continuation-in-part application Serial No. 1,442, filed January 11, 1960.

Application Serial No. 478,922, filed December 30, 1954, in the names of Elkan R. Blout, Marilyn R. Cohler, Milton Greene, Myron S. Simon and Robert B. Wood-

ward, now abandoned and replaced by continuation-in-part application Serial No. 824,785, filed July 3, 1959.

Application Serial No. 612,045, filed September 25, 1956, in the names of Elkan R. Blout, Milton Green and Howard G. Rogers, now abandoned and replaced by continuation-in-part application Serial No. 144,816, filed October 18, 1961.

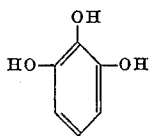
Application Serial No. 612,052, filed September 25, 1956, in the names of Milton Green and Howard G. Rogers, now abandoned and replaced by continuation-in-part Serial No. 165,930, filed January 12, 1962

Application Serial No. 612,053, filed September 25, 1956, in the name of Myron S. Simon.

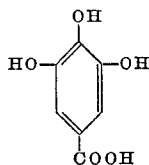
Application Serial No. 612,054, filed September 25, 1956, in the names of Helen P. Husek and Myron S. Simon.

Application Serial No. 612,055, filed September 25, 1956, in the name of Helen P. Husek.

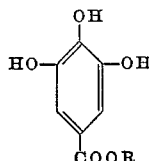
As mentioned above, the compounds which are useful in carrying out the process of this invention are pyrogallol:



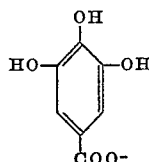
gallic acid:



and esters of gallic acid; the latter may be represented by the formula:



wherein R may be an unsubstituted alkyl, aralkyl or aryl group. When the esters of gallic acid are used as stabilizers, it will be understood that the



radical is the functional portion of the molecule and that the R group may be varied to suit particular needs. For example, when it is desirable to prevent the stabilizer from migrating, the R group may be a higher alkyl. Further, for example, when it is desirable to apply the stabilizer from a particular solvent, R may be varied to provide the desired solubility. Gallic acid and esters of gallic acid are the preferred stabilizers for carrying out the processes of this invention because their oxidation products are appreciably lighter in color than those of pyrogallol and, thus, are less apt to stain the images if oxidized. The preferred gallic acid esters are those in which R is a lower alkyl group, preferably containing one to five carbons. As examples of esters of gallic acid which are useful in carrying out the processes of this invention, mention may be made of ethyl gallate, lauryl gallate, and benzyl gallate.

The amount of stabilizer used will vary with many factors such, for example, as the original color fastness of the dye developers, the amount of sunlight the colored

image will be exposed to during its life expectancy, etc. The amount of stabilizer employed to provide protection may be referred to as an effective amount, i.e., an amount effective to give the desired protection, and it will be understood that such an amount will vary with factors, such as mentioned above, and can be readily determined through color-fading tests which will hereinafter be described. In most cases, swabbing or coating solutions containing about 1 to 2% of stabilizer will be effective in enhancing the color stability of the images.

The following nonlimiting examples illustrate processes within the scope of this invention. Comparative stability is determined in the following examples by accelerated fading tests during which the test images are subjected to intense and extended exposure to sunlamps.

Example 1

An image-receiving element is prepared by coating a cellulose acetate-coated baryta paper with a solution comprising 4% of Nylon Type F8 and 2% gallic acid dissolved in a 4 to 1 mixture (by volume) of isopropanol and water.

A photosensitive element for use with the above image-receiving element is prepared by coating a gelatin-coated cellulose acetate film base with a solution comprising 3% of 2 - [p - (2',5' - dihydroxyphenethyl) - phenylazo] - 4-n-propoxy-1-naphthol and 4% of cellulose acetate hydrogen phthalate dissolved in a 1 to 1 mixture (by volume) of acetone and tetrahydrofuran. After this coating has dried, a silver iodobromide emulsion is applied.

The color transfer image is produced by exposing the photosensitive element, wetting it with an aqueous processing composition comprising:

	Percent
Sodium carboxymethyl cellulose.....	4.5
Potassium bromide.....	0.2
1-phenyl-3-pyrazolidone	0.2
Sodium hydroxide.....	2.0

and superposing it on the image-receiving element. After about one minute, the image-receiving element is stripped from the photosensitive element to reveal the colored image.

Example 2

The procedure of Example 1 is repeated except that ethyl gallate is used in place of the gallic acid.

Example 3

The procedure of Example 1 is repeated except that the gallic acid is not added to the nylon coating solution in preparing the image-receiving element. After processing, the image-receiving element is stripped from the photosensitive element and the image-bearing surface is coated with a solution comprising:

40 cc. of 10% gelatin
10 cc. of methanol
1 gm. of gallic acid

Example 4

The procedure of Example 3 is repeated except that the coating solution comprises:

40 cc. of 10% gelatin
10 cc. of methanol
1 gm. of ethyl gallate

The effectiveness of the stabilizers was tested by exposing the above-obtained images, along with a control transfer image prepared as above in the absence of a stabilizer, to a bank of General Electric 275 watt sunlamps at a distance of 20.5 inches. After an exposure of fifty hours, the color images, having added thereto the stabilizers herein disclosed, showed appreciably less fading than was exhibited by the control image.

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Example 5

An image-receiving element was prepared by coating a gelatin-coated cellulose acetate film base with a 4% solution of Nylon Type F8. The image-receiving element was dyed with 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol to a density of 0.5 to 0.6 and coated with a 10% aqueous gelatin solution containing 1% pyrogallol.

Example 6

An image-receiving element was prepared similar to that in Example 5 except that the pyrogallol was left out of the 10% aqueous gelatin solution.

The image-receiving elements of Examples 5 and 6 were exposed to a bank of General Electric 275 watt sunlamps at a distance of 20.5 inches and the density of the color, at the λ_{\max} of the dye, was measured at various time intervals. Although the pyrogallol caused a slight staining of the image-receiving element of Example 5, the data obtained, which appears in tabular form below, distinctly points out its effectiveness as a stabilizer.

IMAGE-RECEIVING ELEMENT OF EXAMPLE 5
(PYROGALLOL IN GELATIN COATING)

Exposure time (hrs.):	Density
0	0.59
15	0.60
21	0.60
36	0.55
50	0.54

IMAGE-RECEIVING ELEMENT OF EXAMPLE 6 (NO
PYROGALLOL IN GELATIN COATING)

Exposure time (hrs.):	Density
0	0.62
16	0.36
23	0.22
30	0.15
46	Bleached

While it is not known for certain how the stabilizers of this invention function, it is believed that they possess the ability to function both as antioxidants and as ultraviolet light absorbers. The following nonlimiting example illustrates the ability of the stabilizers of this invention to function as antioxidants and ultraviolet light absorbers.

Example 7

A series of image-receiving elements were made up by coating gelatin-subcoated cellulose acetate film bases with a coating solution comprising 4% Nylon Type F8. The resulting image-receiving elements were dyed with 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol dye developer.

Image-receiving element No. 1 was coated with a 10% aqueous gelatin solution containing no stabilizer.

Image-receiving element No. 2 was coated with a 10% aqueous gelatin solution containing 1% ethyl gallate.

Image-receiving element No. 3 was covered with a filter comprising a precast 1 mil sheet of a Nylon Type F8 film which had been coated on its outer surface (i.e., the surface adapted to be most distant from the image-receiving element) with a 10% aqueous gelatin solution containing no stabilizer.

Image-receiving element No. 4 was covered by a filter comprising a sheet of Nylon Type F8, as in image-receiving element No. 3, except that 1% of ethyl gallate was incorporated into the 10% aqueous gelatin solution which was used to coat said Nylon Type F8 sheet.

Image-receiving element No. 5 was covered with a filter, as in image-receiving element No. 4, except that the ethyl gallate in the gelatin coating on the Nylon Type F8 sheet was subjected to aerial oxidation for five days under a General Electric 275 watt sunlamp before it was placed over the image-receiving element.

The above image-receiving elements were exposed to

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a bank of General Electric 275 watt sunlamps at a distance of 20.5 inches, and the densities of the colors were measured at the λ_{\max} of the dye developer at various intervals. The results appear in tabular form below.

DENSITY OF COLOR IN IMAGE-RECEIVING ELEMENTS

Time elapsed	No. 1	No. 2	No. 3	No. 4	No. 5
0 hrs.	0.57	0.575	0.60	0.59	0.46
8 hrs.	0.52	0.60	0.56	0.54	
32 hrs.	0.35	0.60	0.40	0.46	
56 hrs.	0.13	0.53	0.17	0.35	
70 hrs.					0.26
76 hrs.	0.07	0.49	0.08	0.27	

It should be noted in the above table that image-receiving elements No. 1 and No. 3, which contained no stabilizer, were almost completely faded in 76 hours. The best protection was provided in image-receiving element No. 2 wherein the ethyl gallate was intimately associated with the dye developer and could function both as an antioxidant and as an ultraviolet light absorber. From a comparison of the results obtained with image-receiving elements No. 4 and No. 5, it can be concluded that the stabilizers of this invention are capable of functioning as ultraviolet light absorbers in both their reduced and oxidized form. Thus the usefulness of the stabilizers of this invention is not exhausted, when they become oxidized and can no longer function as an antioxidant, for they can continue to provide protection in their oxidized form by acting as ultraviolet light absorbers.

Although the above examples utilize a single dye developer, it is to be understood that this was for purposes of illustration only and that the processes of this invention are equally effective in stabilizing multicolored images produced by processes wherein a plurality of dye developers are used to form the transfer image. As examples of such multicolor processes, mention may be made of the processes disclosed and claimed in the previously mentioned copending application of Howard G. Rogers, and in the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956.

Since certain changes may be made in the above processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a process of forming a photographic image in color wherein a latent image contained in an exposed silver halide emulsion is developed in the presence of a dye developer to provide a predetermined distribution of unoxidized dye developer, and at least part of said distribution of unoxidized dye developer is transferred from said emulsion to a superposed image-receiving layer to provide a positive dye image of the developed image, said dye developer being a compound which is both a dye and a silver halide developing agent, the improvement which comprises increasing the stability of said positive dye image by contacting with said positive dye image with a compound selected from the group consisting of pyrogallol, gallic acid and esters of gallic acid.

2. The process of claim 1 wherein said compound is present in the image-receiving layer prior to formation of said positive dye image.

3. The process of claim 1 wherein said compound is coated over said positive dye image after formation thereof.

4. The process of claim 1 wherein said compound is present in the image-receiving layer prior to formation of said positive dye image and an additional amount is coated over said positive dye image after formation thereof.

5. In a process of forming a photographic image in

color, the steps which comprise developing a latent image contained in an exposed silver halide emulsion with an aqueous alkaline solution containing a dye developer to provide in said emulsion a predetermined distribution of unoxidized dye developer, said dye developer being a compound which is both a dye and a silver halide developing agent, and transferring at least part of said distribution of said unoxidized dye developer from said emulsion to an image-receiving layer in superposed relationship with said emulsion to impart to said image-receiving layer a reversed positive dye image of the developed image, said image-receiving layer having incorporated therein a compound selected from the group consisting of pyrogallol, gallic acid, and esters of gallic acid.

6. A process as defined in claim 5 wherein said compound is gallic acid.

7. A process as defined in claim 5 wherein said compound is ethyl gallate.

8. A process as defined in claim 5 wherein said compound is pyrogallol.

9. A process as defined in claim 5 including the steps, subsequent to the transfer of the unoxidized dye developer to said image-receiving layer, of stripping said image-receiving layer from said emulsion and treating said image-receiving element with a solution comprising a compound selected from the group consisting of pyrogallol, gallic acid, and esters of gallic acid.

10. A process as defined in claim 9 wherein said compound is ethyl gallate.

11. A process as defined in claim 9 wherein said compound is pyrogallol.

12. A process as defined in claim 9 wherein said compound is gallic acid.

13. A process as defined in claim 9 wherein said aqueous solution includes a film-forming material.

14. A process as defined in claim 13 wherein said film-forming material is gelatin.

15. In a process of forming a photographic image in color, the steps which comprise developing a latent image contained in an exposed silver halide emulsion with an aqueous alkaline solution containing a dye developer to

provide in said emulsion a predetermined distribution of unoxidized dye developer, said dye developer being a compound which is both a dye and a silver halide developing agent, transferring at least part of said distribution of said unoxidized dye developer from said emulsion to an image-receiving layer in superposed relationship with said emulsion to impart to said image-receiving layer a reversed positive dye image of the developed image, stripping said image-receiving layer from said emulsion, and treating said image-receiving layer with a solution comprising a compound selected from the group consisting of pyrogallol, gallic acid, and esters of gallic acid.

16. A process as defined in claim 15 wherein said compound is ethyl gallate.

17. A process as defined in claim 15 wherein said solution includes a film-forming material.

18. A process as defined in claim 17 wherein said film-forming material is gelatin.

19. A process as defined in claim 15 wherein said compound is pyrogallol.

20. A process as defined in claim 15 wherein said compound is gallic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,543,181	Land	Feb. 27, 1951
2,747,996	Edgerton et al.	May 29, 1956
2,774,668	Rogers	Dec. 18, 1956
2,892,710	Cohler et al.	June 30, 1959

FOREIGN PATENTS

526,913	Canada	June 26, 1956
9,052	Great Britain	July 22, 1915

OTHER REFERENCES

Henney and Dudley: Handbook of Photography, Whitlesey House, New York, 1939, page 320.

Mees: The Theory of the Photographic Process, Macmillan, New York, 1954, page 547.

Jurd et al.: Journal Org. Chem. 21, 1395-1401 (1956).

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,069,262

December 18, 1962

Howard C. Haas

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 34, for "sliver" read -- silver --;
column 2, line 72, for "Milton Greene" read -- Milton
Green --; column 6, line 61, strike out "with".

Signed and sealed this 24th day of September 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents