

1

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NOVEL PHOTOGRAPHIC PROCESSES

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The present invention relates to photography and more particularly to processes for protecting color diffusion-transfer images from the deleterious 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. 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., compounds which contain, in the same molecule, a silver halide developing function and the 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 layer 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 layer to create thereon the positive dye image. The positive image is preferably viewed by stripping the photosensitive element from the image-receiving layer.

The color fastness of the colored photographic images, produced in such processes, upon prolonged exposure to sunlight often leaves something to be desired. It has been discovered that the color stability of such images in sunlight can be appreciably enhanced by using a salt and especially a halogen salt as a stabilizer. Particularly good results have been obtained from halides selected from the group consisting of the chlorides, iodides and bromides.

The cation portion of the stabilizer may be that of any salt-forming metal. In a preferred embodiment, the cation is an alkali metal, i.e., sodium, potassium, lithium, rubidium and cesium. Especially good results are obtained when the cation of the salt is cesium.

One method of applying the stabilizers herein disclosed comprises treating the finished colored image with a solu-

2

tion comprising the particular salt which is to be employed. The solution may be conveniently applied to the colored image by immersion, swabbing, coating, spraying, flowing, etc. In an especially 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. To insure that the stabilizer will be intimately associated with the dye developers in the image-receiving layer, it is preferable to apply such stabilizers from a solvent which will permeate the image-receiving layer.

Another mode of carrying out the processes of this invention is to incorporate the salt into the image-receiving element prior to their use in the dye developer transfer processes. Such image-receiving elements generally comprise a sheet of dye-receptive material and, in preferred embodiments, comprise a film support bearing a coating of a dyeable material. The salt stabilizer may be incorporated by adding it to the coating solution of dyeable material and applying it therewith to the film support, 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 p-trimethylammonium-p-toluene-sulfonate benzal of polyvinyl alcohol, N-methoxymethyl polyhexamethylene adipamide, polyvinyl alcohol, crosslinked polyvinyl alcohol (i.e., polyvinyl alcohol which has been reacted with a crosslinking 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 salt stabilizers 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 with the dye developers which they are intended to protect.

In an especially useful embodiment of this invention, the salt stabilizers are used in combination with an ultraviolet light absorber. The use of the stabilizers herein disclosed in combination with such absorbers substantially enhances the ability of the latter in protecting the transfer images from the deleterious effects of sunlight. The absorbers may be applied from the same coating solution containing the salt stabilizers or they may be applied separately. When the absorbers are applied separately, methods such for example as those disclosed in the copending application of Howard G. Rogers, Serial No. 786,766, filed January 14, 1959, now abandoned, may be employed. In one such method disclosed therein, the absorbers are incorporated in a permeable, substantially nondyeable layer over the image-receiving layer prior to processing, and during processing the dye developers are transferred through such layers. In another method the absorbers are transferred from the photosensitive element along with the unreacted dye developers.

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 sufficient 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, when the coating solutions comprise a film-forming material, 5.0 to 20% of the halide stabilizer, based on the weight of the polymer, will be effective in

enhancing the color stability of the images. When the coating solution does not contain a film-forming material, use of 5 to 10% solutions of the halide stabilizers gives especially effective results.

The dye developers which are used in the processes, 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 in such dye developers is a hydroquinonyl group. Other suitable developing functions include o-dihydroxyphenyl and o- and p-amino-substituted hydroxyphenyl groups. In general, the developing function is usually supplied by the presence in the molecule of a benzenoid developing radical. 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. 612,045, filed September 25, 1956, in the names of Elkan R. Blout, Milton Green and Howard G. Rogers (now abandoned and replaced by a continuation-in-part thereof, application Serial No. 144,816, filed October 18, 1961) now U.S. Patent No. 3,134,672;

Application Serial No. 612,052, filed September 25, 1956, in the names of Milton Green and Howard G. Rogers (now abandoned and replaced by a continuation-in-part thereof, application Serial No. 165,930, filed January 12, 1962) now U.S. Patent No. 3,135,604;

Application Serial No. 612,053, filed September 25, 1956, in the name of Myron S. Simon (now abandoned and replaced by a continuation-in-part thereof, application Serial No. 196,523, filed May 21, 1962) now U.S. Patent No. 3,183,089;

Application Serial No. 612,054, filed September 25, 1956, in the names of Helen P. Husek and Myron S. Simon (now abandoned and replaced by a continuation-in-part thereof, application Serial No. 197,283, filed May 24, 1962);

Application Serial No. 612,055, filed September 25, 1956, in the name of Helen P. Husek (now abandoned and replaced by a continuation-in-part thereof, application Serial No. 192,355, filed May 4, 1962);

Application Serial No. 755,804, filed August 18, 1958, in the names of Elkan R. Blout, Saul G. Cohen, Milton Green and Myron S. Simon (now abandoned);

Application Serial No. 824,785, filed July 3, 1959, in the names of Elkan R. Blout, Marilyn R. Cohler, Milton Green, Myron S. Simon and Robert B. Woodward (now abandoned and replaced by a continuation-in-part thereof, application Serial No. 233,461, filed October 26, 1962) now U.S. Patent No. 3,135,606;

Application Serial No. 849,727, filed October 30, 1959, in the names of Elkan R. Blout and Myron S. Simon (now abandoned);

Application Serial Nos. 1,442 and 1,443 filed January 11, 1960, in the names of Elkan R. Blout, Saul G. Cohen, Milton Green, Howard G. Rogers, Myron S. Simon and Robert B. Woodward.

The following nonlimiting examples illustrate the effectiveness of the processes of the present invention:

Example 1

Film supports bearing N-methoxymethyl polyhexamethylene adipamide dyeable layers were dyed from 0.086 molar 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-propoxy-1-naphthol, (a magenta dye developer) dye baths containing 2% alkali and 0%, 1%, 5%, 10% and 20% potassium iodide. The dyed sheets were placed 20.5 inches from a battery of six 275 watt General Electric sunlamps spaced 7.5 inches apart. Measurements of

the density and $\lambda_{\max}$ of the dyed sheets after the elapse of various periods of time, showed the following:

(A) 0% KI:

Hours Exposed	Density	$\lambda_{\max}$.
0 hours.....	0.53	530
40 hours.....	0.04	530

(B) 1% KI:

Hours Exposed	Density	$\lambda_{\max}$.
0 hours.....	0.46	530
40 hours.....	0.27	530

(C) 5% KI:

Hours Exposed	Density	$\lambda_{\max}$.
0 hours.....	0.57	530
40 hours.....	0.233	530

(D) 10% KI:

Hours Exposed	Density	$\lambda_{\max}$.
0 hours.....	0.44	530
40 hours.....	0.23	530

(E) 20% KI:

Hours Exposed	Density	$\lambda_{\max}$.
0 hours.....	0.51	530
40 hours.....	0.325	530

Example 2

A film support bearing an N-methoxymethyl polyhexamethylene adipamide dyeable layer was soaked in saturated potassium iodide and then dyed in a 0.086 molar 2 - [p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-propoxy-1-naphthol dye bath containing 2% alkali for 15 seconds. Measurements of the density and $\lambda_{\max}$ of the sheet after various periods of exposure to the battery of sunlamps showed the following:

Hours Exposed	Density	$\lambda_{\max}$.
0 hours.....	0.64	530
40 hours.....	0.335	530

Example 3

A film support bearing a N-methoxymethyl polyhexamethylene adipamide dyeable layer was dyed in a 0.086 molar 2 - [p - (2',5' - dihydroxyphenethyl)-phenylazo]-4-propoxy-1-naphthol dye bath containing 2% alkali for 15 seconds and then soaked in a saturated potassium iodide bath for 30 minutes. Upon exposure to a battery of sunlamps in a manner similar to that employed in Example 1 the following changes in density were observed:

Hours Exposed	Density	$\lambda_{\max}$.
0 hours.....	0.54	530
40 hours.....	0.43	530
86 hours.....	0.365	530
146 hours.....	0.31	530

Example 4

A film structure prepared and dyed in a manner similar to that employed in Example 3 was coated with a 4:1 ethyl alcohol-water solution comprising 20% N-methoxy-

5

methyl polyhexamethylene adipamide and 2% potassium iodide. Upon exposure to the battery of sunlamps mentioned above, the following results were obtained:

Hours Exposed	Density	λ_{max} .
0 hours.....	0.66	530
24 hours.....	0.619	530
48 hours.....	0.54	530
72 hours.....	0.49	530

Example 5

A film structure was dyed and coated in a manner similar to that employed in Example 4 except that 2% potassium bromide was used in place of the potassium iodide in the adipamide coating solution. Upon exposure to the battery of sunlamps, the following changes in density were observed:

Hours Exposed	Density	λ_{max} .
0 hours.....	0.61	530
24 hours.....	0.46	530
48 hours.....	0.22	530

Example 6

A series of dyed film structures similar to those employed in Example 4 were coated with the following 4:1 ethyl alcohol-water coating solutions comprising:

Film structure (a):	Percent
N-methoxymethyl polyhexamethylene adipamide	20
Uvinul 490 (trade name of Antara Chemicals, a division of General Aniline & Film Corp., New York, N.Y., for a substituted benzophenone ultraviolet light absorber)	2.0
Film structure (b):	
N-methoxymethyl polyhexamethylene adipamide	20
Uvinul 490	2.0
Potassium iodide	2.0
Film structure (c):	
N-methoxymethyl polyhexamethylene adipamide	20
Potassium iodide	2.0
Agent At-316 (trade name of Antara Chemicals for a substituted benzophenone ultraviolet light absorber)	Saturated solution
Film structure (d):	
N-methoxymethyl polyhexamethylene adipamide	20
Potassium iodide	2.0
T.B.S. (trade name of Dow Chemical Co., Midland, Michigan for a 4-tert-butylphenyl salicylate ultraviolet light absorber)	Saturated solution

Upon exposure to the battery of sunlamps the following results were obtained:

Film structure (a)—Uvinul 490:

Hours Exposed	Density	λ_{max} .
0 hours.....	0.55	530
72 hours.....	0.28	530
144 hours.....	0.12	530

Film structure (b)—Uvinul 490 and 2.0% KI:

Hours Exposed	Density	λ_{max} .
0 hours.....	0.60	530
72 hours.....	0.55	530
144 hours.....	0.42	530

6

Film structure (c)—Agent At-316 and 2.0% KI:

Hours Exposed	Density	λ_{max} .
0 hours.....	0.76	530
72 hours.....	0.75	530

Film structure (d)—TBS and 2.0% KI:

Hours Exposed	Density	λ_{max} .
0 hours.....	0.91	530
72 hours.....	0.84	530

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.

Image-receiving elements having image-receiving layers of the p-trimethylammonium-p-toluene-sulfonate benzal of polyvinyl alcohol and bearing multicolor step-wedge-images, produced through processes such as disclosed in the above-mentioned copending applications of Edwin H. Land and Howard G. Rogers with the use of the above-mentioned 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-propoxy - 1 - naphthol (magenta dye developer) along with 1,4-bis-[β - (2',5' - dihydroxyphenyl)-isopropylamino]-5,8-dihydroxyanthraquinone (a cyan dye developer) and 1 - phenyl - 3 - N-n-hexyl-carbamyl-4-[p-(2',5' - dihydroxyphenethyl) - phenylazo] - 5 - pyrazolone (a yellow dye developer) were coated with the following coating solutions: (1) a coating comprising 1% lithium bromide and 10% gelatin, (2) a coating solution comprising 1% cesium bromide and 10% gelatin and (3) a coating solution comprising 1% lithium chloride and 10% gelatin. The image-receiving elements along with a control were exposed to an Atlas Fadeometer, equipped with a Xenon arc. After 96 hours of exposure it was observed that the light stabilities of the images treated with the stabilizers of this invention were substantially better than that of the untreated control.

Other halides which were tested on multicolor step-wedge-images such as mentioned above and were found effective in improving the light stability are lithium bromide, calcium chloride, cadmium bromide, cadmium chloride, magnesium bromide, calcium bromide, magnesium chloride, sodium bromide, cesium chloride, and sodium chloride.

Other non-halide salts which have been found effective as stabilizers but which appear to be not as effective as the halide salts were ammonium sulfate and aluminum sulfate.

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 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 photographed image, the improvement which comprises increasing the stability of said positive

dye image by treating said positive dye image, subsequent to its formation, with a halide salt of an alkali metal.

2. The process as defined in claim 1 wherein said halide salt is selected from the group consisting of iodides, chlorides and bromides.

3. A process as defined in claim 2 wherein said halide salt is an iodide.

4. A process as defined in claim 3 wherein said iodide is potassium iodide.

5. A process as defined in claim 2 wherein said halide salt is a bromide.

6. A process as defined in claim 2 wherein said halide salt is a chloride.

7. A process as defined in claim 1 wherein said halide salt is used in combination with an organic ultraviolet light absorber.

8. In a process of forming a photographic image in color, the steps which comprise developing 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, 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 halide salt of an alkali metal, whereby the stability of said positive dye image is increased.

9. A process as defined in claim 8 wherein said halide salt is selected from the group consisting of iodides, bromides and chlorides.

10. A process as defined in claim 9 wherein said halide salt is an iodide.

11. A process as defined in claim 9 wherein said halide salt is a bromide.

12. A process as defined in claim 9 wherein said halide salt is a chloride.

13. A process as defined in claim 8 wherein said halide salt is used in combination with an organic ultraviolet light absorber.

14. A process as defined in claim 8 including the steps, subsequent to the transfer of the unoxidized dye developer to said image-receiving layer, of separating said image-receiving layer from said emulsion and treating

said image-receiving layer with a solution comprising said halide salt.

15. In a process of forming a photographic image in color, the steps which comprise developing 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, 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 potassium iodide.

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