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3,239,338

PHOTOGRAPHIC PROCESS

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

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.

My copending U.S. application, Serial No. 748,421, filed July 14, 1958, now U.S. Patent No. 2,983,606, discloses and claims processes wherein dye developers (i.e., compounds which are both dyes and silver halide developing agents) 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 image-wise 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 a superposed image-receiving layer to create thereon the positive dye image. The positive dye image is preferably viewed by stripping the photosensitive element from the image-receiving layer.

The image-receiving elements used in such processes generally comprise an opaque or transparent support coated with an image-receiving layer of a dyeable material which is permeable to the alkaline aqueous processing solution. In the past, film-forming materials such as polyvinyl alcohol, gelatin and nylons, such as N-methoxymethyl polyhexamethylene adipamide, have been used as the dyeable materials.

The color fastness of the colored photographic images produced in such processes, upon prolonged exposure to sunlight, ultraviolet light, etc., often leaves something to be desired. I have found that, when the image-receiving layer on which the image is formed comprises at least in part polyvinyl alcohol, polyvinyl alcohol copolymers or derivatives of polyvinyl alcohol having unreacted hydroxyl groups, the color fastness of the images may be substantially enhanced by treating said images, subse-

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quent to their formation, with a boron compound which in an aqueous solution forms a borate ion. The boron compound may conveniently be applied to the colored image by immersion, swabbing, coating, spraying, flowing, etc. When desired, the solution may also comprise a film-forming polymer, such, for example, as gelatin, polyvinyl alcohol, etc., 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. In a preferred embodiment, the boron compounds are applied from aqueous solutions. When desired, such aqueous solutions may contain organic solvents such, for example, as methanol, acetone, etc.

In a particularly useful embodiment of this invention, enhanced image stability has been obtained where the solution providing the borate ion also includes a saccharide, e.g., fructose or anhydroennaheptitol. As also mentioned above, said solution may also contain a film material, e.g., polyvinyl alcohol. In another very useful embodiment, the inclusion of the di-ortho tolyl guanidine salt of dicatechol borate has been found to enhance the stabilizing effect of the borate ion, particularly when used with aqueous boric acid or with aqueous boric acid containing anhydroennaheptitol and polyvinyl alcohol.

In the preparation of image-receiving elements having image-receiving layers comprising polyvinyl alcohol or derivatives thereof, borate ions are sometimes used to reduce the water-sensitivity of the image-receiving layers prior to the use of the elements in diffusion transfer processes. Such prior use of the borate ions has no noticeable effect on the stability of the images which are formed thereon and should be distinguished from the processes of the present invention wherein the borate ions are used subsequent to the formation of the image.

The dye developers, from which the images are formed, may also be defined as 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 are o-dihydroxyphenyl radicals. In general, the developing function includes a benzenoid developing function. Examples of representative dye developers are given in my previously mentioned application, Serial No. 748,421. Additional useful dye developers are described in the following copending U.S. applications:

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

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. 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.

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).

Application Serial No. 612,045, filed September 25, 1956, in the names of Elkan R. Blout, Milton Green and Howard G. Rogers (now abandoned).

Application Serial No. 612,052, filed September 25, 1956, in the names of Milton Green and Howard G. Rogers (now abandoned).

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

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

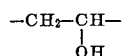
Application Serial No. 612,055, filed September 25, 1956, in the name of Helen P. Husek (now abandoned).

The processes of this invention have been found especially useful in stabilizing transfer images formed from azo and anthraquinone dye developers.

As mentioned above, the stabilizers of this invention are boron compounds which in water form a borate ion. Such borate ions may be completely or only partially ionized, that is, they can have a negative valence of 1, 2 or 3, e.g., BO_3^- , HBO_3^- , H_2BO_3^- , NaBO_3^- or Na_2BO_3^- . As examples of compounds which will provide such borate ions, mention may be made of orthoboric acid H_3BO_3 (boric acid), metaboric acid HBO_3 , tetraboric acid $\text{H}_2\text{B}_4\text{O}_7$, perboric acid HBO_3 , the alkali metal and other water-soluble salts of said acids, e.g., borax, $\text{Na}_2\text{B}_4\text{O}_7$; potassium borate K_3BO_3 , sodium perborate NaBO_3 and boric acid esters, e.g., an ester of boric acid and ethylene glycol.

The processes of this invention, as set forth above, are especially effective in stabilizing dye developer transfer images which are produced on image-receiving layers comprising polyvinyl alcohol, copolymers of polyvinyl alcohol and derivatives of polyvinyl alcohol having free hydroxyl groups. The image-receiving layer need not comprise solely the above-mentioned polyvinyl alcohol polymers, but may comprise other polymers and other reagents, e.g., mordants, pH buffers, etc., which may be useful in the transfer processes. Especially useful results have been obtained, however, when said image-receiving layers comprise a major portion of such polymers. As examples of other polymers which have been found useful, mention may be made of poly-4-vinylpyridine, poly-N-vinylpyrrolidone, and nylons such, for example, as N-methoxymethyl polyhexamethylene adipamide.

By the term "derivatives of polyvinyl alcohol" is meant polymers which can be converted to polyvinyl alcohol through hydrolysis. As examples of such derivatives, mention may be made of the partial esters and acetals such as partially hydrolyzed polyvinyl acetate, a partial acetal of polyvinyl alcohol and 4-pyridine carboxaldehyde and a partial acetal of polyvinyl alcohol and p-trimethylaminobenzaldehyde p-toluene sulfonate. When the image-receiving layer comprises copolymers of vinyl alcohol or derivatives of polyvinyl alcohol, it is desirable for best results that such copolymers and derivatives comprise a major portion of



segments.

The amount of boron compound 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 the boron compound will be effective in enhancing the color stability of the images.

The following nonlimiting examples illustrate the preparation of image-receiving elements for use in the processes of the present invention:

Example 1

A subcoated film support was coated with a methanol-water solution (1 to 9 by volume comprising):

	Percent
p-Trimethylammonium benzaldehyde p-toluene sulfonate partial acetal of polyvinyl alcohol -----	7.5
1-phenyl-5-mercaptotetrazole (first dissolved in a 1 to 9, by volume, methanol-water solution) --	0.053
Sodium perborate -----	0.01

Example 2

A subcoated film support was coated with an aqueous coating solution comprising:

	Percent
Elevanol 72-60 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for high molecular weight completely hydrolyzed polyvinyl alcohol) -----	2.4
p-Trimethylammonium benzaldehyde p-toluene sulfonate partial acetal of polyvinyl alcohol -----	2.4
1-phenyl-5-mercaptotetrazole (first dissolved in a 1 to 9, by volume, methanol-water solution) ----	0.08
Sodium perborate -----	0.01
Boric acid -----	0.01

and a small amount of a nonionic wetting agent.

Example 3

A subcoated film support was coated with a coating solution comprising:

	Cc.
10% Elvanol 72-60 solution -----	12
10% aqueous solution of poly-4-vinylpyridine (containing a small amount of acetic acid to facilitate solubilization) -----	8
1-phenyl-5-mercaptotetrazole (first dissolved in a 1 to 9, by volume, methanol-water solution) -----	0.4
Water containing a drop of a nonionic wetting agent	50

Example 4

A subcoated film support was coated with a coating solution comprising:

10% aqueous polyvinyl alcohol solution -----cc--	12
10% aqueous solution of a partial acetal of polyvinyl alcohol and p-trimethylammonium benzaldehyde p-toluene sulfonate -----cc--	12
N-methoxymethyl polyhexamethylene adipamide (dissolved in 30 cc. of isopropanol and 5 cc. of water) -----gm--	0.48
1-phenyl-5-mercaptotetrazole (first dissolved in a 1 to 9, by volume, methanol-water solution) cc--	0.4
2% boric acid solution -----cc--	0.25
2% sodium perborate solution -----cc--	0.25

Example 5

A subcoated film support was coated with an aqueous coating solution comprising:

	Percent
Polyvinyl alcohol -----	4.8
1-phenyl-5-mercaptotetrazole (first dissolved in a 1 to 9, by volume, methanol-water solution) ----	0.08
Sodium perborate -----	0.01

and a small amount of a nonionic wetting agent.

The image-receiving elements prepared in the above examples were used in diffusion transfer processes employing multilayer photosensitive elements prepared in a manner similar to that disclosed in the above-mentioned copending application Serial No. 748,421 (now U.S. Patent No. 2,983,606). In general, the photosensitive elements comprised a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum; said emulsions having disposed in separate alkali-permeable layers behind them, re-

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spectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. The particular dye developers employed in the photosensitive elements were (1) 1,4-bis- $[\alpha$ -methyl- β -(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone (a cyan dye developer), (2) 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-propoxy-1-naphthol (a magenta dye developer), and (3) 1-phenyl-3-n-hexyl carboxamido-4-[p-(hydroquinonyl-ethyl)-phenylazo]-5-pyrazolone (a yellow dye developer). Areas of the photosensitive elements were exposed to (1) blue and green light only, (2) red and blue light only, and (3) red and green light only. After the transfer process, one set of the image-receiving elements was swabbed with a 2% aqueous boric acid solution, and a second set was left unswabbed.

The effectiveness of the processes of this invention was shown by (1) measuring, by reflectance, the integral densities of the transfer images using red, green and blue filters, (2) subjecting the images to wet xenon arc tests, and (3) again measuring the integral densities after 20 and 40 hours of exposure to show the percentage fading. The results appear in tabular form below:

IMAGE-RECEIVING ELEMENT OF EXAMPLE 1
[Percent fading]

	Unswabbed		Swabbed	
	20 Hours	40 Hours	20 Hours	40 Hours
Red Filter.....	30	49	8	12.5
Green Filter.....	81	91	40	50
Blue Filter.....	71	77	72	78

IMAGE-RECEIVING ELEMENT OF EXAMPLE 2
[Percent fading]

	Unswabbed		Swabbed	
	20 Hours	40 Hours	20 Hours	40 Hours
Red Filter.....	45	67	7	9
Green Filter.....	91	96	40	56
Blue Filter.....	78	85	55	64.5

IMAGE-RECEIVING ELEMENT OF EXAMPLE 3
[Percent fading]

	Unswabbed		Swabbed	
	20 Hours	40 Hours	20 Hours	40 Hours
Red Filter.....	40	58	8	16
Green Filter.....	80	94	24	51
Blue Filter.....	70	89	46	74

IMAGE-RECEIVING ELEMENT OF EXAMPLE 4
[Percent fading]

	Unswabbed		Swabbed	
	20 Hours	40 Hours	20 Hours	40 Hours
Red Filter.....	46	62	-----	16
Green Filter.....	87	89	53	53
Blue Filter.....	60	70	55	66

IMAGE-RECEIVING ELEMENT OF EXAMPLE 5
[Percent fading]

	Unswabbed		Swabbed	
	20 Hours	40 Hours	20 Hours	40 Hours
Red Filter.....	49	64.5	5	6
Green Filter.....	85	96	52	47
Blue Filter.....	72	83	50	59

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The effectiveness of sodium tetraborate and sodium perborate was also demonstrated by tests similar to those performed above.

When desired, the boron compound may be used in a latent form and placed in the image-receiving element prior to the use of such element in a diffusion transfer process. During processing, such boron compound may be rendered active by the processing solution to provide borate ions to stabilize the image. One example of such a latent boron compound is a hydrolyzable borate ester.

It also has been found that the stabilizing effects of treatment with a boron compound which forms a borate ion in aqueous solution appear to be increased where the transfer process has been performed in the presence of a quaternary ammonium compound, as disclosed in my copending application, Serial No. 50,851, filed August 22, 1960, now U.S. Patent No. 3,173,786, and particularly N- β -phenethyl- α -picolinium bromide or N-benzyl- α -picolinium bromide. An increased effect also has been observed where the transfer process has been effected in the presence of such a quaternary ammonium compound in combination with a substituted hydroquinone auxiliary silver halide developing agent, particularly 4'-methylphenyl-hydroquinone.

Since certain changes may be made in the above process 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, said dye developer being a compound which is both a dye and a silver halide developing agent, and wherein at least part of said distribution of said unoxidized dye developer is transferred from said emulsion to a superposed image-receiving layer to provide a dye image thereon, the improvement which comprises increasing the stability of said dye image when it is formed on an image-receiving layer which comprises a film-forming material selected from the group consisting of polyvinyl alcohol, polyvinyl alcohol copolymers and derivatives of polyvinyl alcohol having unreacted hydroxy groups, by treating said dye images, subsequent to their formation, with a boron compound which forms a borate ion in aqueous solution.

2. A process as defined in claim 1 wherein said boron compound is applied to said image from an aqueous solution.

3. A process as defined in claim 1 wherein said boron compound is boric acid.

4. A process as defined in claim 1 wherein said compound is sodium tetraborate.

5. A process as defined in claim 1 wherein said image is swabbed with an aqueous solution of boric acid.

6. A process as defined in claim 1 wherein said film-forming material comprises a mixture of polyvinyl alcohol and poly-4-vinylpyridine.

7. A process as defined in claim 1 wherein said film-forming material comprises a mixture of polyvinyl alcohol and a partial acetal of polyvinyl alcohol and p-trimethylammonium benzaldehyde p-toluene sulfonate.

8. A process as defined in claim 2 wherein said aqueous solution contains polyvinyl alcohol.

9. A process as defined in claim 1 wherein the development is carried out in the presence of a quaternary ammonium salt.

10. A process as defined in claim 1 wherein said dye developer is selected from the group consisting of azo and anthraquinone dye developers.

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