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PHOTOGRAPHIC PRODUCTS AND PROCESSES

Howard G. Rogers, Weston, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

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This invention relates to photography and more particularly to novel photographic products and processes.

One object of this invention is to provide novel image-receiving elements for use in color diffusion transfer processes.

Another object of this invention is to provide novel color diffusion transfer processes utilizing said image-receiving elements.

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, and the product possessing the features, properties and the relation of elements 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 present invention is concerned with color diffusion transfer processes and more particularly with color diffusion transfer processes employing dye developers such as disclosed in U.S. Patent 2,983,606, issued May 9, 1961 to Howard G. Rogers. Dye developers are compounds which contain in the same molecule both the chromophoric system of a dye and also a silver halide developing function. They may be further defined as dyes which are silver halide developing agents. In such color diffusion transfer processes a latent silver halide image in a photosensitive element is developed in the presence of a dye developer and, as a result of this development, the dye developer in the exposed areas is oxidized and substantially immobilized. At least a portion of the immobilization is believed to be due in part to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards to its solubility in alkaline solutions. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in a liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element. The image-receiving element receives a depthwise diffusion from the developed emulsion of unoxidized dye developer, without appreciably disturbing the imagewise distribution thereof to provide a reversed image of the developed image.

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 it has been proposed to use film-forming materials such as polyvinyl alcohol and nylons such as N-methoxymethyl polyhexamethylene adipamide. Image-receiving materials embodying poly-4-vinylpyridine, and particularly a mixture of polyvinyl alcohol and poly-4-vinylpyridine, have been found especially useful and form the subject matter of the copending application of Howard C. Haas, Serial No. 50,848, filed August 22, 1960 (now U.S. Patent No. 3,148,061,

issued September 8, 1964). The present invention is concerned with providing improved image-receiving elements of the latter type.

Usually when poly-4-vinylpyridine or mixtures of polyvinyl alcohol and poly-4-vinylpyridine are used as the image-receiving materials, dense transfer images having relatively good stability to light are obtained. Despite the relatively good stability there is still room for improvement. It has now been found that a substantial increase in the stability to light of the images may be obtained by applying a thin overcoat of polyvinyl alcohol over the image-receiving layer comprising poly-4-vinylpyridine. The light stability, based on percent fading in accelerated fading tests, is substantially better than that obtained on an image-receiving layer comprising poly-4-vinylpyridine or a mixture of polyvinyl alcohol and poly-4-vinylpyridine. That the thin layer of polyvinyl alcohol would cooperate with the underlying image-receiving layer to provide such an improvetment is quite unexpected.

Usually the thickness of the thin polyvinyl alcohol overcoat layer may be varied over a considerable range. Generally the lower limit is the minimum effective amount of polyvinyl alcohol and the maximum limit lies below that concentration at which the polyvinyl alcohol layer would be serving as the image-receiving layer. Generally the use of between about 50 mg. to 200 mg. per square foot will provide effective results. In a preferred embodiment about 75 to 175 mg. per square foot are employed. Especially good results have been obtained using about 100 mg. per square foot.

When it is desirable to use a mixture of polyvinyl alcohol and poly-4-vinylpyridine as the underlying image-receiving layer, the ratio of polyvinyl alcohol to poly-4-vinylpyridine may generally be varied to suit particular needs. Generally the use of about 1 to 9 parts, by weight, of polyvinyl alcohol to 1 part, by weight, of the poly-4-vinylpyridine will give effective results. Especially good results are obtained when the ratio of polyvinyl alcohol to polyvinylpyridine is about 2:1.

The novel image-receiving elements within this invention may be prepared by coating a sheet of a suitable film support such, for example, as cellulose acetate, cellulose nitrate or cellulose acetate-coated baryta paper, which may be suitably subcoated for proper adhesion, with a solution, preferably a 3 to 10% solution, comprising the poly-4-vinylpyridine or a mixture of polyvinyl alcohol and the poly-4-vinylpyridine and subsequently applying a thin polyvinyl alcohol layer. Although poly-4-vinylpyridine is not soluble in water the coating may be applied from aqueous solutions by using a small amount of acid in the coating solution. In a preferred embodiment, volatile acids such as, for example, formic, acetic, etc., are used in applying the coatings. Evaporation of such volatile acids when the image-receiving element is cast renders said image-receiving layers less water-sensitive. Generally the coating and drying operations involved in preparing the image-receiving elements may be carried out by techniques commonly employed in the art.

The term poly-4-vinylpyridine polymers as used herein refers to polymers comprising a major portion of segments derived from 4-vinylpyridine monomer and more preferably to homopolymers of 4-vinylpyridine.

Polyvinylpyridine polymers for use in the image-receiving layers of this invention may be prepared by the simple polymerization of 4-vinylpyridine monomers. The polyvinyl alcohols for use in the layers may be selected from the various partially and completely hydrolyzed materials of this nature which are commercially available. As examples of suitable polyvinyl alcohols, mention may be made of those commercially available under the names Elvanol 72-60 (trade name of E. I. du Pont de Nemours

and Company, Wilmington, Delaware) and Gelvatol 2–75 (trade name of Shawinigan Products Corporation, New York, New York).

As set forth above, the dye developers which are provided with increased light stability by the image-receiving elements of this invention are dyes which are also silver halide developing agents. Examples representing the dye developers are given in the previously-mentioned U. S. Patent No. 2,983,606 of Howard G. Rogers and the copending application of Howard C. Haas, Serial No. 50,848 (now U.S. Patent No. 3,148,061, issued September 8, 1964).

When desired, the polyvinyl alcohol-poly-4-vinylpyridine layers and the polyvinyl alcohol overcoat layer may be treated with suitable hardeners or cross-linking agents to reduce the water sensitivity of the polyvinyl alcohol. As examples of such materials, mention may be made of boric acid and glyoxal, as well as acrolein and acrolein condensates whose use is disclosed and claimed in the copending application of Lloyd D. Taylor, Serial No. 229,194, filed October 8, 1962.

The effectiveness of the image-receiving elements of the present invention is especially noticeable when the transfer image is treated subsequent to its formation with borate ions such as disclosed in the copending application of Howard G. Rogers, Serial No. 93,309, filed March 6, 1961 (now U.S. Patent No. 3,239,338, issued March 8, 1966).

The following nonlimiting examples illustrate the preparation of image-receiving elements within the scope of the present invention.

EXAMPLE 1

A sheet of subcoated baryta paper was coated with an aqueous solution containing a small amount of acetic acid and comprising the following:

	Percent
Polyvinyl alcohol (Elvanol 72–60)	3.2
Poly-4-vinylpyridine	1.6
1-phenyl-5-mercaptotetrazole (first dissolved in a 1:9, by volume, methanol-water solution)	0.08
Boric acid	0.01

to provide a layer having a coverage of approximately 600 mg./ft.^{2}. After drying, the resulting layer was then coated with a 2% aqueous solution of polyvinyl alcohol containing 0.01% boric acid to provide an overcoat layer comprising 100 mg./ft.^{2} of polyvinyl alcohol.

EXAMPLE 2

An image-receiving element was prepared as in Example 1 except that the polyvinyl alcohol overcoat layer comprised 200 mg./ft.^{2}.

EXAMPLE 3

An image-receiving element was prepared as in Example 1 except that the polyvinyl alcohol overcoat layer comprised 150 mg./ft.^{2} of polyvinyl alcohol.

A control image-receiving element was prepared in a manner similar to that of Example 1 except that the polyvinyl alcohol overcoat layer was eliminated.

The image-receiving elements prepared in the above examples along wtih the control were used in diffusion transfer processes employing multilayer photosensitive elements prepared in a manner similar to that disclosed in my above-mentioned 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 stratum and a blue-sensitive silver halide stratum; said emulsions having disposed in a separate alkali-permeable layer behind them, respectively, 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-[α-methyl-β - (2′,5′ - dihydroxyphenyl) - ethylamino] - 5,8 - dihydroxy - anthraquinone (a cyan dye developer), (2) 2 - [p - (2′,5′ - dihydroxyphenethyl) - phenylazo] - 4-iso - propoxy - 1 - napthol (a magenta dye developer) and (3) 1 - phenyl - 3 - N - n - hexyl carboxamido - 4-[p - (hydroquinonylethyl) - 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 transfer, the image-receiving elements and the controls were swabbed with an aqueous solution comprising about 3% boric acid.

The effectiveness of the image-receiving elements of the present invention was shown by (1) measuring, by reflectance, the initial integral densities of the transfer images using a green filter, (2) subjecting the images to high humidity xenon arc accelerated fading tests, and (3) again measuring the integral density through a green filter after 20, 40 and 100 hours of exposure to show the percentage of magenta fading. The results appear in tabular form below:

Image-receiving element of Example 1

Time elapsed:	Fading, percent
20 hours	14
40 hours	18
100 hours	25

Image-receiving element of Example 2

Time elapsed:	
20 hours	4
40 hours	14
100 hours	23

Image-receiving element of Example 3

Time elapsed:	
20 hours	3
40 hours	12
100 hours	23

Control

Time elapsed:	
20 hours	24
40 hours	33
100 hours	46

It should be noted that the above tests clearly show that the stability of the transfer images produced on the image-receiving elements of the present invention is substantially better than that of those produced on similar image-receiving layers which do not have the polyvinyl alcohol overcoat.

Examination of photomicrographs of cross-sections of the polyvinyl alcohol-overcoated image-receiving elements of the above examples showed that there was essentially no dye in the polyvinyl alcohol overcoat. This result was unexpected in view of the fact that polyvinyl alcohol per se may be used as an image-receiving layer.

The polyvinyl alcohol overcoat of this invention also has been found effective in imparting increased light stability to dye images formed on image-receiving elements containing a polymeric acid interlayer; for example, an overcoat of polyvinyl alcohol has been useful with image-receiving elements prepared as described in the copending application of Edwin H. Land, Serial No. 234,864, filed November 1, 1962, and particularly as described in Examples 10 and 21 of said copending application.

It will be noted that the polyvinyl alcohol overcoat may contain reagents which further increase light stability, e.g., an ultraviolet absorber, as contemplated in my copending application, Serial No. 786,766, filed January 14, 1959 (now abandoned, the subject matter of which has been incorporated in Serial No. 354,963, filed March 26, 1964), or other reagents which improve image quality.

The image-receiving elements of this invention are especially useful in composite film units intended for use in a Polaroid Land Camera, made by Polaroid Corporation, Cambridge 39, Massachusetts, or a similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on February 10, 1948. In general, such com-

posite film units comprise a photosensitive element, an image-receiving element and a rupturable pod containing an aqueous alkaline processing solution. The elements and pod are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pod may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of the pods used in such rolls are well known to the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

It is apparent that by selecting a film base from among suitable known opaque and transparent materials, reflection or transparent prints may be obtained.

It should be noted that other materials useful in the diffusion transfer processes may be incorporated into the image-receiving layer. As examples of such materials, mention may be made of dye mordants, antifoggants, oxidizing agents, and acids and alkalies for pH adjustments.

Since certain changes may be made in the above products and 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. As a novel photographic product for color diffusion transfer processes employing dye developers, an image-receiving element comprising a support bearing an inner layer comprising an image-receiving material selected from the group consisting of poly-4-vinylpyridine and mixtures of poly-4-vinylpyridine and polyvinyl alcohol and having a thin outer layer of about 50 to 200 mg. per square foot of polyvinyl alcohol.

2. A product as defined in claim 1, wherein said outer layer comprises 75 to about 175 mg. of polyvinyl alcohol per square foot.

3. A product as defined in claim 2, wherein said outer layer comprises about 100 mg. per square foot of polyvinyl alcohol.

4. A product as defined in claim 1, wherein said image-receiving material of said inner layer comprises a mixture of polyvinyl alcohol and poly-4-vinylpyridine and about 1 to 9 parts, by weight, of polyvinyl alcohol are present for about 1 part, by weight, of the poly-4-vinylpyridine.

5. A product as defined in claim 4, wherein said inner layer comprises about 2 parts of polyvinyl alcohol, by weight, to about 1 part of poly-4-vinylpyridine, by weight.

6. 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 an imagewise distribution of unoxidized dye developer and at least a portion of said imagewise distribution of said unoxidized developer is transferred, by imbibition, from said emulsion to an image-receiving element in superposed relationship with said emulsion to impart thereto in said image-receiving element a positive dye image, the improvement characterized by the feature that said image-receiving element comprises a support bearing an inner layer comprising an image-receiving material selected from the group consisting of poly-4-vinylpyridine and mixtures of polyvinyl alcohol and poly-4-vinylpyridine and a thin outer layer of about 50 to 200 mg. per square foot of polyvinyl alcohol, said transferred dye developer being transferred through said outer layer of polyvinyl alcohol to said inner layer.

7. A process as defined in claim 6, wherein said outer layer comprises 75 to about 175 mg. of polyvinyl alcohol per square foot.

8. A process as defined in claim 6, wherein said outer layer comprises about 100 mg. per square foot of polyvinyl alcohol.

9. A process as defined in claim 7, wherein said image-receiving material of said inner layer comprises a mixture of polyvinyl alcohol and poly-4-vinylpyridine and about 1 to 9 parts, by weight, of polyvinyl alcohol are present for about 1 part, by weight, of the poly-4-vinylpyridine.

10. A process as defined in claim 9, wherein said inner layer comprises about 2 parts of polyvinyl alcohol, by weight, to about 1 part of poly-4-vinylpyridine, by weight.

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NORMAN G. TORCHIN, *Primary Examiner.*

J. TRAVIS BROWN, *Examiner.*