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ETHYL ACRYLATE, METHYL METHACRYLATE AND ACRYLIC ACID TERPOLYMER ADHESIVE FOR POLYESTER FILM SUPPORTS AND GELATIN LAYERS

Henry S. Kolesinski, Burlington, and Peter H. Roth, Needham, Mass., assignors to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

The adhesion of a felatinous layer to a polyester film support may be facilitated by coating said support prior to application of said gelatinous layer with a terpolymer comprising ethyl acrylate, methyl methacrylate, and acrylic acid.

The present invention is concerned with diffusion transfer processes and, more particularly, with photosensitive elements for use in said diffusion transfer processes.

U.S. Patent No. 2,983,606 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 the dye developer and an imagewise distribution of unreacted dye developer is formed in unexposed areas. At least a portion of said unreacted dye developer is transferred to a superposed image-receiving layer to provide the transfer image thereon.

Multicolor transfer images may be produced by such processes by using photosensitive elements such as those claimed and disclosed in the copending U.S. application of Edwin H. Land and Howard G. Rogers, Ser. No. 565,135, filed Feb. 13, 1956, now U.S. Patent No. 3,345,163 wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed with a single processing solution and transferred to a common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halid emulsion stratum, and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer, and a yellow dye developer.

In a preferred mode of carrying out both the monochromatic and multicolor processes, the dye developers are disposed, prior to exposure, in a separate alkali-permeable layer behind the silver halide emulsion with which it is associated, i.e., on the side of the emulsion which is most distant from the photographed subject when the emulsion is exposed, and preferably also adapted to be most distant from the image-receiving layer when in superposed relation therewith. In especially useful embodiments the dye developer is first dissolved in a water immiscible solvent such as diethyl lauramide and then dispersed in the alkali-permeable polymer. Illustrative of such photosensitive elements is a multicolor negative comprising (1) a support which is coated in turn on one side with (2) a gelatin layer having dispersed therein a cyan dye developer which is dissolved in water immiscible solvent, (3) a red-sensitive silver halide emulsion layer, (4) a gelatin or synthetic polymer interlayer, (5) a gelatin layer having dispersed therein a magenta dye developer which is dissolved in a water immiscible solvent, (6) a green-sensitive silver halide emulsion, (7) a gelatin or

synthetic polymer interlayer (8) a gelatin layer having dispersed therein a yellow dye developer which is dissolved in a water immiscible solvent, and (9) a blue-sensitive silver halide emulsion.

In the past, materials such as cellulose acetate have been employed as the film support. Although said cellulose acetate provides satisfactory results, it is desirable, in certain instances, to use a polyester film support such as Mylar (trade name of E. I. du Pont de Nemours & Company, Wilmington, Del., for an ethyleneglycolterephthalic acid polyester). The use of such polyesters is accomplished, however, by disadvantages, e.g., it is generally only available commercially as a clear film and it is necessary to apply an opaque layer over it, when for example, it is intended to be used in film packs, such as disclosed in U.S. Patent No. 3,002,437 wherein development takes place outside the camera. Another disadvantage is that its adhesion to gelatin leaves much to be desired and usually it has to be surface treated, e.g., with a chromic acid-sulfuric acid solution. The adhesive problem is especially acute when the gelatin layer comprising the dye developer is immediately adjacent the film support. In such embodiments the dye developer, which is generally present in substantial amounts (usually at least 1:1 by weight to the gelatin) and is often dissolved in a water immiscible solvent, has an adverse effect on adhesion and it is usually necessary to further sub-coat the film support. As can be seen, these disadvantages necessitate the use of special surface treatments and additional coating operations.

It has been found in the present invention that if a terpolymer of ethyl acrylate, methyl methacrylate and acrylic acid is employed as the polymeric binder for the opacifier that the resulting opaque layer will be firmly adhered to the Mylar and possess excellent subbing properties for the adjacent dye developer-gelatin layer. As can be seen, the use of such terpolymers eliminates the need for the surface treatment and sub-coating steps. Moreover, the use of the opaque layer on the same side of the support as the photosensitive element, further reduces the possibility of leaks due to light piping.

The results in the present invention are especially unexpected when the opacifier is present in the opaque layer in at least a 1:1 ratio by weight to the terpolymer and the amount of dye developer in the adjacent gelatin layer is also at least 1:1 by weight to the gelatin. Under such adverse conditions the fact that any adhesion at all is obtained, yet alone good adhesion, is quite surprising.

One object of the present invention is to provide novel photosensitive elements for dye developer diffusion transfer processes.

Another object of the present invention is to provide novel photosensitive element for dye developer diffusion transfer processes having a layer of a terpolymer of ethyl acrylate, methyl methacrylate and acrylic acid adjacent a polyester film support, which layer serves both as a binder for an opacifier and as a subbing layer for the film support.

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

The invention accordingly comprises the product possessing the features, properties and the relation of components 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.

Generally the terpolymers which are used in the combined opacifying and subbing layers of the present inven-

tion comprise about 55 to 75% by weight of ethyl acrylate, about 20 to 40% by weight of methyl methacrylate and 2 to 6% by weight of acrylic acid. Terpolymers comprising about 60% ethyl acrylate, about 36% methyl methacrylate and about 4% acrylic acid have been found particularly useful.

In an especially useful embodiment of the present invention the terpolymer layer also comprises a polymer selected from the group consisting of gelatin and polyvinyl alcohol. Such an embodiment has been found particularly useful when the dye developers in the adjoining gelatin layer are dissolved in a water immiscible solvent and are dispersed in this state in the gelatin layer. The addition of the polyvinyl alcohol and gelatin polymers has been found particularly effective in increasing the solvent resistance of the terpolymer layer and preventing the dye developers from migrating thereinto. Although the amount of gelatin or polyvinyl alcohol may be varied, particularly good results were obtained when they were present in amounts of about 15 to 30% by weight of the terpolymer. Especially good results were obtained when about 25% of said polymers were employed.

The terpolymers for use in the present invention may be prepared by well-known polymerization techniques, e.g., bulk, solvent, etc. In especially useful embodiments, the polymers are prepared by emulsion polymerization, e.g., dispersing the monomers, at room temperature, with vigorous stirring in an aqueous solution comprising an emulsifying or dispersing agent such as sodium lauryl sulfate and adding a redox catalyst. The resulting emulsion may be compounded directly with the opacifier and used in this form in the coating operation.

Generally, the opacifiers for use in the photographic elements of the present invention may be selected from the various pigments available, e.g., titanium dioxide, carbon black, etc., which have the required covering power and are inert to the photographic agents. Especially useful results have been obtained with carbon blacks. In using such carbon blacks it has been found advantageous to pre-disperse them in aqueous solutions before compounding them with the terpolymer emulsion. Generally, the amount of pigment used will vary depending on the covering power of the particular pigment employed. Usually about 300 to 1200 mgms. of the pigment per square foot and more particularly about 600 mgms. will provide adequate covering power. Generally the ratio of pigment, e.g., carbon black, to terpolymer will be at least 1 to 1 by weight, and more particularly about 2 to 1.

The photosensitive elements of the present invention are particularly useful in film packs, such as disclosed in the above-mentioned U.S. Patent No. 3,002,437, where development takes place outside the camera. Generally, such film packs include a plurality of film units, each comprising a photosensitive sheet, a second sheet adapted to be superposed with the photosensitive sheet following exposure thereof for receiving the image, a container of a fluid processing composition adapted to be distributed between the superposed photosensitive and second sheets to effect the processing thereof, and leader means for moving the photosensitive and second sheets into superposition and in engagement with means for distributing the processing fluid.

The following nonlimiting examples illustrate the preparation of coating solutions for use in preparing the photosensitive elements of the present invention:

EXAMPLE A

Carbon black-terpolymer dispersion

An emulsion of a terpolymer comprising about 60% by weight ethyl acrylate, 36% by weight methyl methacrylate and about 4% by weight of acrylic acid was added to a diluted 25% by weight carbon black dispersion (Aquablack M, sold by Columbia Carbon Co.), comprising 1% by weight (based on the carbon black) of Alkanol B (trademark of E. I. du Pont de Nemours & Company for an alkylnaphthalene sodium sulfonate wetting agent) until the ratio of carbon black to terpolymer was about 2 to 1 by weight. The resulting dispersion, which contained about 15% by weight of carbon black and had a surface tension of 38 dynes/cm., was filtered through 3 sheets of 325 mesh stainless steel screen.

EXAMPLE B

Cyan dye developer-gelatin dispersion

1 part by weight of 1,4-bis-[α-methyl-β-hydroquinonylethylamino]-5,8-dihydroxyanthraquinone (a cyan dye developer) was dissolved in 2 parts of diethyl lauramide and was dispersed by means of a colloidal mill in a solution comprising 0.9 part gelatin, 5.1 parts water and 0.5 part Alkanol B.

The following nonlimiting example illustrates the preparation of a photosensitive element within the scope of the present invention.

EXAMPLE 1

An unsubbed sheet of Mylar was successively coated with:

(1) A carbon black-terpolymer layer comprising about 600 mgs. of carbon per square foot (dispersion of Example A).

(2) A cyan dye developer-gelatin layer (dispersion of Example B).

(3) A red-sensitive silver iodobromide emulsion layer.

(4) A gelatin interlayer.

(5) A gelatin layer having dispersed therein in a water-immiscible solvent a magenta dye developer, e.g., 2-[p-(2′,5′ - dihydroxyphenethyl-phenylazo]-4-isopropoxy-1-naphthol.

(6) A green-sensitive silver iodobromide emulsion layer.

(7) A gelatin interlayer.

(8) A gelatin layer having dispersed therein in a water-immiscible solvent a yellow dye developer, e.g., 1-phenyl-3 - N - n - hexylcarbamyl - 4 - [p-(2′,5′-dihydroxyphenethyl)-phenylazo]-5-pyrazolone.

(9) A blue-sensitive silver iodobromide emulsion layer.

When the above photosensitive element was incorporated in a film pack, such as disclosed in the above-mentioned U.S. Patent No. 3,002,437, and processed outside the camera, the carbon black-terpolymer layer was substantially impermeable to the alkali, had no apparent photographic activity and provided good protection from light. No signs of delamination between the Mylar, terpolymer, and cyan dye developer layers were observed.

EXAMPLE 2

A photosensitive element was prepared in a manner similar to Example 1 except that the terpolymer layer also comprised 25% by weight (based on the terpolymer) of gelatin.

EXAMPLE 3

A photosensitive element was prepared in a manner similar to Example 1 except that the terpolymer layer also comprised 25% by weight (based on the terpolymer) of polyvinyl alcohol.

When the photosensitive elements prepared in Examples 2 and 3 were tested in a manner similar to the photosensitive elements of Example 1, they provided equally good results. In addition, they provided enhanced resistance to the solvent and substantially reduced dye developer migration.

In the above examples the carbon black-terpolymer layer was produced in a single coating step. For added insurance against light leaks, said layer may be applied in several coating steps, e.g., two coatings comprising 300 mgs. of carbon per square foot.

Since certain changes may be made in the above product 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. A photosensitive element comprising a polyester film support bearing on one side (a) an immediate adjoining terpolymer layer comprising an opacifier, said terpolymer comprising by weight about 55 to 75% ethyl acrylate, about 20 to 40% of methyl methacrylate and about 2 to 6% acrylic acid; (b) a gelatin layer comprising a dye developer adjoining said terpolymer layer and (c) a silver halide emulsion layer.

2. A photosensitive element as defined in claim 1 wherein the ratio of opacifier to terpolymer in said terpolymer layer is at least 1 to 1 by weight.

3. A photosensitive element as defined in claim 1 wherein the ratio of dye developer to gelatin in said gelatin layer is at least 1 to 1 by weight.

4. A photosensitive element as defined in claim 2 wherein the ratio of dye developer to gelatin in said gelatin layer is at least 1 to 1 by weight.

5. A photosensitive element comprising a polyester film support bearing on one side (a) an immediately adjoining terpolymer layer comprising carbon black pigment, said terpolymer comprising by weight about 55 to 75% of ethyl acrylate, 20 to 40% of methyl methacrylate and 2 to 6% acrylic acid, the ratio of carbon black to terpolymer in said layer being at least 1 to 1 by weight; (b) a gelatin layer comprising a dye developer adjoining said terpolymer layer, the ratio of dye developer to gelatin in said gelatin layer being at least 1 to 1 by weight; and (c) a silver halide emulsion layer.

6. A photosensitive element as defined in claim 5 wherein said terpolymer comprises by weight about 60% ethyl acrylate, about 36% methyl methacrylate and about 4% acrylic acid.

7. A photosensitive element comprising a polyester film support bearing on one side (a) an immediately adjoining terpolymer layer comprising an opacifier and a polymer selected from the group consisting of gelatin and polyvinyl alcohol, said terpolymer comprising by weight about 55 to 75% ethyl acrylate, about 20 to 40% of methyl methacrylate and about 2 to 6% acrylic acid; (b) a gelatin layer comprising a dye developer adjoining said terpolymer layer; and (c) a silver halide emulsion layer.

8. A photosensitive element as defined in claim 7 wherein said dye developer is dispersed in said gelatin layer as a solution of said dye developer in a water immiscible solvent.

9. A photosensitive element as defined in claim 7 wherein the ratio of opacifier to terpolymer in said terpolymer layer is at least 1 to 1 by weight and the ratio of dye developer to gelatin in said gelatin layer is at least 1 to 1 by weight.

10. A photosensitive element as defined in claim 8 wherein the ratio of opacifier to terpolymer in said terpolymer layer is at least 1 to 1 by weight and the ratio of dye developer to gelatin in said gelatin layer is at least 1 to 1 by weight.

11. A photosensitive element as defined in claim 10 wherein said gelatin and polyvinyl alcohol are present in said terpolymer in amounts ranging between about 15 to 30% by weight of said terpolymer.

12. A photosensitive element as defined in claim 8 wherein said opacifier is carbon black.

13. A photosensitive element as defined in claim 10 wherein said opacifier is carbon black.

References Cited

UNITED STATES PATENTS

2,875,056	2/1959	Smith et al.	96—87
3,249,457	5/1966	Lynch	117—161 XR

NORMAN G. TORCHIN, Primary Examiner

J. R. EVERETT, JR., Assistant Examiner

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117—138, 161