July 17, 1962 H. C. HAAS 3,044,873

PHOTOGRAPHIC PRODUCTS AND PROCESSES

Filed Dec. 17, 1958

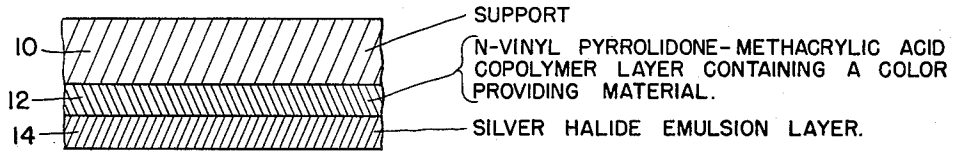


FIG. 1

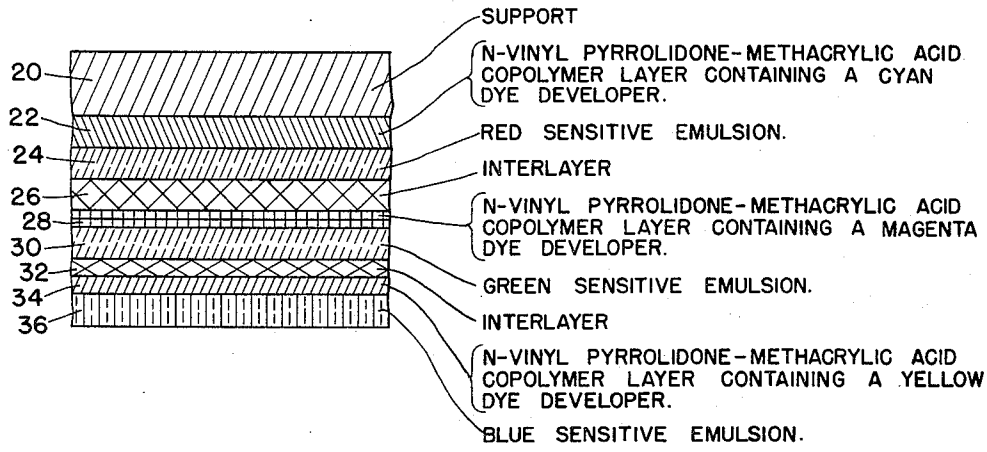


FIG. 2

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United States Patent Office 3,044,873 Patented July 17, 1962

3,044,873

PHOTOGRAPHIC PRODUCTS AND PROCESSES

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Filed Dec. 17, 1958, Ser. No. 781,007
18 Claims. (Cl. 96—29)

The present invention is concerned with photography and more particularly with novel photosensitive elements for color diffusion transfer processes.

One object of this invention is to provide novel photosensitive elements for color diffusion transfer processes comprising at least one silver halide emulsion layer and at least one layer of a polymeric material having a color-providing material disposed therein, said polymeric material being selected from the group consisting of (*a*) copolymers of N-vinyl pyrrolidone and an α,β-unsaturated carboxylic acid and (*b*) terpolymers of N-vinyl pyrrolidone, an α,β-unsaturated carboxylic acid, and a lower alkyl ester of said α,β-unsaturated carboxylic acids.

Another object of this invention is to provide improved color diffusion transfer processes utilizing said photosensitive elements.

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

The invention accordingly comprises 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 taken in connection with the accompanying drawing wherein:

FIGURE 1 is a diagrammatic cross-sectional view of one embodiment of a photosensitive element of this invention; and

FIG. 2 is a diagrammatic cross-sectional view of one embodiment of a multilayer photosensitive element within the scope of the invention.

The present invention is particularly related to color diffusion transfer processes. In such processes a photosensitive element including a silver halide emulsion layer is exposed to create therein a latent image. The latent image is developed and, concurrent with and under the control of this development, an imagewise distribution of mobile color-providing materials is formed. At least a portion of these color-providing materials is transferred by means of an alkaline aqueous processing liquid to a superposed image-receiving material to form a colored image thereon. As examples of such processes, mention may be made of the processes claimed and disclosed in the copending application of Howard G. Rogers, Serial No. 748,421, filed July 14, 1958, which is a continuation-in-part of application Serial No. 415,073, filed March 9, 1954 (now abandoned), said continuation-in-part application now U.S. Patent No. 2,983,606, issued May 9, 1961, wherein dye developers (i.e., compounds which contain in the same molecule both the chromophoric system of a dye and also a silver halide developing function) are the color-providing materials, the processes claimed and disclosed in U.S. Patent No. 2,647,049, issued July 28, 1953, to Edwin H. Land wherein color developers are employed to develop the latent image and color couplers are the color-providing materials, and the processes disclosed in U.S. Patent No. 2,774,668, issued December 18, 1956, to Howard G. Rogers, wherein complete, preformed dyes are used as the color-providing substances.

In an especially useful mode of carrying out color diffusion transfer processes, such as described above, the color-providing materials are disposed in a separate alkali-permeable layer in the photosensitive element. The separate alkali-permeable layer may be placed either in front of or behind the photosensitive emulsion with which it is associated; however, in a preferred embodiment it is placed behind, i.e., on the side of the emulsion which is most distant from the photographed subject when the emulsion is exposed, and preferably also is adapted to be most distant from the image-receiving element when in superposed relation therewith. In carrying out the processes, the photosensitive element is exposed and wetted with an aqueous alkaline processing solution, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element is superposed prior to, during or after wetting on an image-receiving element. In a preferred embodiment, the aqueous alkaline processing solution contains a viscosity-increasing compound and is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed position with the image-receiving element. The alkaline aqueous processing solution permeates the photosensitive emulsion and alkali-permeable layers and solubilizes the color-providing materials to provide a substantially uniform distribution of the color-providing materials therein. As the processes proceed, the exposed silver halide image is developed and the color-providing materials in the exposed areas are immobilized or precipitated, thereby providing an imagewise distribution of mobile color-providing materials in the unexposed areas. At least a portion of the color-providing materials in the unexposed areas is transferred and imbibed on the image-receiving element to form the positive image thereon. The positive image produced is preferably viewed by stripping the image-receiving element from the photosensitive element.

When the color-providing materials are incorporated into a separate alkali-permeable layer, it is desirable that said alkali-permeable layer have good dry adhesion to the other layers present in order to withstand the stresses and strains such a layer would be normally subjected to during, for example, coating operations and especially to withstand the stresses and strains which are encountered if the photosensitive element is part of a roll film unit. Such adhesion must be achieved in the presence of relatively high amounts of the color-providing materials which generally have little or no adhesiveness in themselves and which often have an adverse effect on the bonding. It is further desirable, and no less important, that the alkali-permeable layer have good wet adhesion to the other layers present; otherwise, during processing, upon stripping the image-receiving element from the photosensitive element, delamination may take place and portions of the photosensitive element would adhere to the surface of the image-receiving element and mar the quality of the transfer image. It is still further desirable that the alkali-permeable layer readily release the color-providing materials in order to make the maximum amount of said materials available for forming the positive image. In the past, film-forming polymers such, for example, as cellulose acetate hydrogen phthalate have been proposed as materials for the alkali-permeable layers.

It has been discovered that when the color-providing materials are disposed in a layer comprising (*a*) a copolymer made from N-vinyl pyrrolidone and an α,β-unsaturated carboxylic acid or (*b*) a terpolymer made from N-vinyl pyrrolidone, an α,β-unsaturated carboxylic acid, and a lower alkyl ester of an α,β-unsaturated carboxylic acid, said copolymers and terpolymers provide wet and dry adhesion which is superior to that obtained with cellulose acetate hydrogen phthalate and, further, said

copolymers and terpolymers readily release the color-providing materials.

The usefulness of the copolymers of this invention is especially demonstrable when dye developers are the color-providing materials. 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 radical which is capable of developing an exposed silver halide image, e.g., a benzenoid developing radical. A preferred silver halide developing radical in such compounds is a hydroquinonyl group. Examples of representative dye developers are given in the previously mentioned application of Howard G. Rogers, Serial No. 748,421. Additional useful dye developers are described in the following copending applications:

Application Serial No. 449,514, filed August 12, 1954, in the names of Elkan R. Blout and Myron S. Simon.

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.

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

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

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

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.

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.

In color diffusion transfer processes employing dye developers, the dye developer, as mentioned previously for color-providing substances, in general, is preferably placed in a separate alkali-permeable layer behind the photosensitive layer. Upon processing, the alkaline aqueous processing solution permeates to said alkali-permeable layer and solubilizes the dye developer therefrom. As the process proceeds, the dye developer is oxidized as a result of the development of the exposed areas and is immobilized. At least a portion of the unreacted dye developer is imbibed on a superposed image-receiving material to create thereon the positive dye image. In such processes the immobilization of the dye developers in the exposed areas is apparently due, at least in part, to a change in the solubility characteristics of the dye developer upon oxidation. It may also be due, in part, to a tanning effect on the emulsion by the oxidized developer, and to localized exhaustion of alkali in exposed areas as a result of development.

FIG. 1 of the accompanying drawing illustrates one embodiment of a photosensitive element for use in color diffusion transfer processes wherein a copolymer of N-vinyl pyrrolidone and methacrylic acid is used as the material for a separate alkali-permeable layer. The photosensitive element shown therein comprises a support **10**, a layer **12** of N-vinyl pyrrolidone-methacrylic acid containing a color-providing substance and a photosensitive layer **14**.

In preparing photosensitive elements of the type mentioned above and in preparing other photosensitive elements within the scope of this invention, the polymeric layers may be conveniently applied from coating solutions containing the desired polymers. The preferred coating solutions comprise 2 to 10% of polymer; however, this amount may be varied to suit particular needs. The coating and drying operations may be carried out according to procedures well known to the art. The color-providing substances which are to be disposed in the separate alkali-permeable layer may be incorporated into the coating solution and applied therewith, or they may be imbibed onto the layer after its application. When the color-providing materials are incorporated into the coating solutions, they may be dispersed or solubilized therein, depending upon the form desired for use in the diffusion transfer processes, the solvent, the color-providing material, etc. As an example of a suitable solvent for use in preparing the photosensitive elements of this invention, mention may be made of 90% ethanol and methanol-tetrahydrofuran mixtures. When the coating solution is applied directly to a support such, for example, as baryta, cellulose acetate, etc., said support may be first subcoated with a suitable material such, for example, as gelatin to further enhance the adhesion.

When the solubility permits, e.g., when the polymers contain a high ratio of the α,β-unsaturated carboxylic acid, water may be used as the solvent in the coating solutions. The color-providing substances, if not water soluble, may be dispersed directly into the aqueous coating solutions or they may be first dissolved in an organic water-immiscible solvent and then dispersed in the coating solution.

The N-vinyl pyrrolidone copolymers and terpolymers of this invention are also suitable as alkali-permeable materials in integral multilayer photosensitive elements for use in multicolor diffusion transfer processes. As an example of such photosensitive elements, mention may be made of the photosensitive elements disclosed and claimed in the copending application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation with a single common image receiving element. A suitable arrangement of this type comprises 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 associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. In one of the preferred embodiments of photosensitive elements of this type, the dye developers are disposed in separate alkali-permeable layers behind the photosensitive silver halide emulsion stratum with which they are associated. As in monochromatic photosensitive elements, the N-vinyl pyrrolidone copolymers and terpolymers of this invention, when used as the alkali-permeable layer, provide superior wet and dry adhesion, as compared with cellulose acetate hydrogen phthalate. When the copolymers and terpolymers of this invention are used in such multicolor film units, at least one of the color-providing materials is disposed in a layer comprising a copolymer or terpolymer of this invention. However, it should be understood that in certain instances it may be desirable, for reasons such, for example, as permeation rates, transfer rates, etc., to dispose some of the color-providing materials in the silver halide emulsion layers or in alkali-permeable layers of materials other than those disclosed herein.

A multilayer photosensitive element of the type mentioned above is illustrated in FIG. 2 of the accompanying drawing. A support **20** carries a layer **22** of N-vinyl pyrrolidone-methacrylic acid copolymer containing a cyan dye developer; a layer **24** of a red-sensitive silver halide emulsion; an interlayer **26**, e.g., polyvinyl alcohol, gelatin, etc., a layer **28** of a N-vinyl pyrrolidone-methacrylic acid copolymer containing a magenta dye developer; a layer **30** of a green-sensitive silver halide emulsion; an interlayer **32**; a layer **34** of a N-vinyl pyrrolidone-meth-

acrylic acid copolymer containing a yellow dye developer; and an outermost layer **36** of a blue-sensitive silver halide emulsion. In certain instances, for example when the yellow dye developer is not of the appropriate color or is not present in a state capable of functioning as a filter, a yellow filter may be placed in interlayer 32.

Although the N-vinyl pyrrolidone-methacrylic acid copolymer layers in the photosensitive element of FIG. 2 are shown principally adhered to gelatin or polyvinyl alcohol layers, it should be noted that the copolymers and terpolymers of this invention show good adhesion to hydrophilic, alkali-permeable, film-forming materials in general. As a result of this, wide discretion may be exercised in selecting film-forming materials as carriers for the silver halide emulsion, interlayers, and other layers which may be adjacent to the copolymer and terpolymer layers disclosed herein. For example, one may replace gelatin, which is the carrier usually used in the silver halide emulsion layers, in whole or in part with gelatin substitutes such, for example, as cellulose ethers, polyvinyl alcohols, partially hydrolyzed organic esters of polyvinyl alcohols, acetals of polyvinyl alcohols, etc. Similar discretion may be exercised in selecting the film-forming materials for the interlayers and other layers. In certain instances, if desired, the copolymers and terpolymers of this invention may be used as the carrier in the interlayers, and other layers which may be present.

Although the copolymers and terpolymers of this invention provide good adhesion by themselves, in certain instances their adhesion to adjacent layers may be enhanced by incorporating a small amount of said copolymers or terpolymers into the layers to which they are to be adhered. The amount of copolymer or terpolymer so incorporated may be varied to suit particular needs; generally, however, an amount comprising about 10%, by weight, of the adjacent carrier material will provide the increased adhesion.

Both the monochromatic and multicolor photosensitive elements within the scope of this invention may be used in roll film units which contain a plurality of photosensitive elements. The photosensitive elements of this invention are especially useful in multiple film units intended for use in a "Polaroid Land Camera," sold by Polariod Corporation, Cambridge, Massachusetts, or similar structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717. In general, such film units comprise a photosensitive roll, a roll of image-receiving material, and a plurality of pods containing an aqueous alkaline processing solution. The rolls and pods 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 processing solution between the superposed elements. The nature and construction of the pods used in such units are well known to the art. See, for example, U.S. Patent Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

The N-vinyl pyrrolidone copolymers and terpolymers for use in preparing the novel photosensitive elements of this invention may be prepared by polymerizing N-vinyl pyrrolidone with the designated monomers in the presence of a suitable catalyst such, for example, as azobisisobutyronitrile. The preferred α,β-unsaturated carboxylic acids for use in preparing the copolymers of this invention are those which contain less than six carbon atoms. As examples of suitable α,β-unsaturated carboxylic acids, mention may be made of acrylic, methacrylic, α-chloroacrylic, crotonic, etc. The preferred lower alkyl esters for preparing the terpolymers contain less than five carbon atoms in the alkyl chain and, more particularly, less than three carbon atoms. As examples of lower alkyl esters of α,β-unsaturated carboxylic acid esters which are useful in preparing the terpolymers of this invention, mention may be made of methyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, etc. In polymerizing the N-vinyl pyrrolidone copolymers and terpolymers of this invention, the mole fraction of N-vinyl pyrrolidone monomer used to prepare the polymers may be varied to suit particular needs; however, the preferred copolymers and terpolymers are those in which N-vinyl pyrrolidone constitutes a mole fraction of the reactants of at least 0.5. The copolymers which have been found to be particularly useful are those which are prepared by using about a 9 to 1 molar ratio of N-vinyl pyrrolidone monomer to the other comonomer used. The terpolymers which have been found to be particularly useful are those wherein the mole fractions of N-vinyl pyrrolidone monomer, the α,β-unsaturated carboxylic acid monomer and the lower alkyl ester monomer, used to prepare the terpolymers, are about 0.64, 0.11 and 0.25, respectively.

It will be understood that if the reaction rates of the monomers are not substantially equal, the composition of the polymers produced at different stages of the reaction will vary. The polymers which have been found to be particularly useful are the initial polymers produced.

The following nonlimiting examples illustrate the preparation of copolymers and terpolymers for use in preparing the novel photosensitive elements of this invention.

Example 1

9.0 gms. of distilled methacrylic acid, 5.0 gms. of distilled N-vinyl pyrrolidone (7 to 3 molar ratio), 0.07 gm. of azobisisobutyronitrile and 14 ml. of benzene were placed in a tube and the tube was evacuated and sealed under vacuum. The materials were reacted at 70° C. for one hour and the resulting polymeric precipitate was filtered, washed with hexane and dried under vacuum. The N-vinyl pyrrolidone-methacrylic acid copolymer produced was soluble in 2% alkali (sodium hydroxide) methanol, 95% ethanol and acetone-water (1 to 1, by volume).

Example 2

7.8 gms. of distilled N-vinyl pyrrolidone, 2.6 gms. of distilled methacrylic acid (7 to 3 molar ratio), 0.52 gm. of azobisisobutyronitrile and 10 ml. of benzene were placed in a tube and the tube was evacuated and sealed under vacuum. The materials were reacted at 70° C. for one hour and the resulting polymeric precipitate was filtered, washed with hexane and dried under vacuum. The N-vinyl pyrrolidone-methacrylic acid copolymer produced was soluble in 2% alkali and 95% ethanol.

Example 3

38.09 gms. of N-vinyl pyrrolidone and 2.74 gms. of acrylic acid (9 to 1 molar ratio) were dissolved in 30 ml. of benzene containing 0.0815 gm. of benzoyl peroxide and polymerized under vacuum at 60° C. for ten minutes. The resulting polymer, which precipitated from the reaction medium, was separated, washed with hexane and dried under vacuum. It was soluble in methanol, methanol and water, methyl Cellosolve and 2% aqueous alkali.

Example 4

31.10 gms. of N-vinyl pyrrolidone and 8.64 gms. of acrylic acid (7 to 3 molar ratio) were dissolved in 30 ml. of benzene containing 0.0795 gm. of benzoyl peroxide and polymerized under vacuum at 60° C. for ten minutes. The resulting polymer, which was insoluble in the reaction medium, was separated, washed with hexane and dried under vacuum. Its solubility properties were similar to those of the polymer produced in Example 3.

Example 5

24.7 gms. of N-vinyl pyrrolidone and 16.0 gms. of acrylic acid (1 to 1 molar ratio) were dissolved in 50 ml. of benzene containing 0.0204 gm. of benzoyl peroxide and polymerized under nitrogen at 60° C. for ten minutes. The resulting polymer, which was insoluble in the reaction medium, was separated, washed with hexane and dried under vacuum.

Example 6

15.85 gms. of N-vinyl pyrrolidone and 24.0 gms. of acrylic acid (3 to 7 molar ratio) were dissolved in 50 ml. of benzene containing 0.03 gm. of benzoyl peroxide and polymerized under nitrogen at 60° C. for ten minutes. The resulting polymer, which was insoluble in the reaction medium, was separated, washed with hexane and dried under vacuum.

Example 7

19.4 gms. of N-vinyl pyrrolidone, 2.3 gms. of acrylic acid and 6.4 gms. of methyl acrylate (6 to 1 to 2.5 molar ratio) were dissolved in 60 ml. of benzene containing 0.084 gm. of azobisisobutyronitrile and heated at 60° C. under nitrogen. Rapid polymerization took place, and the resulting polymer was precipitated into hexane, filtered and washed with hexane. The polymer was purified by dissolving it in a mixture of methanol and chloroform and precipitating it into ether. It was soluble in 2% alkali, methanol-chloroform mixtures and swelled in water.

The following nonlimiting examples illustrate the preparation of photosensitive elements within the scope of this invention and their use in color diffusion transfer processes.

Example 8

A methanol-ethylene glycol monomethyl ether (4 to 1, by volume) coating solution comprising 4% of N-vinyl pyrrolidone-methacrylic acid copolymer (prepared as in Example 1) and 1.5% of 1-phenyl-3-N-n-hexyl-carboxamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone (prepared by the processes disclosed in the copending application of Elkan R. Blout, Milton Green and Howard G. Rogers, Serial No. 612,045, filed September 25, 1956) was coated on a gelatin-coated cellulose acetate support. When the coating solution had dried, a coating of silver iodobromide emulsion was applied.

The above photosensitive element was exposed and then processed by spreading an aqueous processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	5.0
Sodium hydroxide	3.0
1-phenyl-3-pyrazolidone	0.8
6-nitrobenzimidazole	0.12
2,5-bis-ethyleneiminohydroquinone	0.6

between said photosensitive element and an image-receiving element as said elements were brought into superposed relationship. The image-receiving element comprised a cellulose acetate-coated baryta paper which had been coated with an ethanol solution containing 4% of Nylon Type F 8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for N-methoxymethyl polyhexamethylene adipamide). After an imbibition period of approximately one minute, the image-receiving element was separated and contained a dense yellow positive dye image of the photographed subject. No signs of delamination in the photosensitive element were observed.

Example 9

A photosensitive element similar to that of Example 8 was prepared using the N-vinyl pyrrolidone-methacrylic acid copolymer prepared in Example 2. Upon processing, in a manner similar to that employed in Example 8, a dense yellow positive dye image of the photographed subject was obtained. No signs of delamination in the photosensitive element were observed.

Example 10

A methanol-tetrahydrofuran (3 to 1, by volume) coating solution comprising 2% of a N-vinyl pyrrolidone-acrylic acid copolymer (prepared as in Example 3) and 3% of 1-phenyl-3-N-n-hexyl-carboxamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone was coated on a gelatin-coated cellulose acetate support. When the coating solution had dried, a coating of silver iodobromide emulsion was applied. Upon exposing and processing, in a manner similar to that employed in Example 8, a dense yellow positive dye image of the photographed subject was obtained with no signs of delamination.

Example 11

A photosensitive element, similar to that of Example 8, was prepared using a N-vinyl pyrrolidone-acrylic acid copolymer as prepared in Example 5. Upon exposing and processing, in a manner similar to that employed in Example 8, a dense yellow positive dye image was obtained and no signs of delamination were observed.

Example 12

A photosensitive element, similar to that of Example 8, was prepared using a N-vinyl pyrrolidone-acrylic acid copolymer prepared as in Example 6. Upon exposing and processing, in a manner similar to that employed in Example 8, a dense yellow positive image was obtained and no signs of delamination were observed.

Example 13

A photosensitive element was made up, in a manner similar to that employed in Example 8, using a methanol-ethylene glycol monomethyl ether (1 to 1, by volume) coating solution comprising 2% of a N-vinyl pyrrolidone-acrylic acid copolymer, prepared as in Example 4, and 3% of 1-phenyl-3-N-n-hexyl-carboxamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone. Upon exposing and processing, in a manner similar to that employed in Example 8, a dense positive yellow image was obtained and no signs of delamination were observed.

Example 14

A photosensitive element was made up, in a manner similar to that employed in Example 8, using a coating solution comprising 2% of a N-vinyl pyrrolidone-acrylic acid-methyl acrylate terpolymer, as prepared in Example 7 and 3% of 1-phenyl-3-N-n-hexyl-carboxamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone dissolved in a methanol-tetrahydrofuran solvent (1 to 1, by volume). Upon exposing and processing, in a manner similar to that employed in Example 8, a dense positive yellow image was obtained and no signs of delamination were observed.

In the above example, the dry adhesion of the copolymer and terpolymer layers was tested by adhering a strip of an adhesive film, e.g., cellophane tape, to the photosensitive element, stripping it from the element, and observing for delamination. Each of the photosensitive elements, prepared in the above examples, was superior to similar photosensitive elements prepared with cellulose acetate hydrogen phthalate as the dye carrier. The dry adhesion was further tested by bending the photosensitive elements over rods of various diameters and observing for delamination. In each instance, the photosensitive elements of this invention could be bent to a sharper angle than similar elements using cellulose acetate hydrogen phthalate without showing signs of delamination.

As mentioned previously, the polymers of this invention may be used in integral multilayer photosensitive elements such as those disclosed in the previously mentioned copending application Serial No. 748,421. As examples of suitable coating solutions which may be used to apply the cyan, magenta and yellow dye developer layers in such elements, mention may be made of:

(1) A tetrahydrofuran-methanol solution (1 to 3, by volume) comprising 5.5% of 1,4-bis-[β-(2',5'-dihydroxyphenyl)-isopropylamino]-anthraquinone (a cyan dye developer) and 2% of a N-vinyl pyrrolidone-acrylic acid copolymer as prepared in Example 3.

(2) A tetrahydrofuran-methanol solution (1 to 3, by volume) comprising 3.5% of 2-[p-(2',5'-dihydroxyphenethyl) - phenylazo] - 4-n-propoxy-1-naphthol (a magenta

dye developer) and 2% of a N-vinyl pyrrolidone-acrylic acid copolymer, prepared as in Example 3.

(3) A tetrahydrofuran-methanol solution (1 to 3, by volume) comprising 3% of 1-phenyl-3-N-n-hexyl-carbamyl-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone and 2% of a N-vinyl pyrrolidone-acrylic acid copolymer as prepared in Example 3.

The N-vinyl pyrrolidone copolymers and terpolymers within the scope of this invention are further suitable for use in screen-type photosensitive elements, such as disclosed in the aforementioned application of Howard G. Rogers, Serial No. 748,421 and also the copending application of Edwin H. Land, Serial No. 448,441, filed August 9, 1954, wherein at least two selectively sensitized silver halide emulsions are arranged in the form of a screen and the color-providing substances, as in multilayer photosensitive elements, are preferably placed in a separate alkali-permeable layer in back of the photosensitive emulsion with which they are associated.

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

What is claimed is:

1. A photosensitive element comprising a support bearing in turn on one surface a polymeric layer having a color-providing material selected from the group consisting of dyes and dye intermediates disposed therein, and an outer silver halide emulsion layer; said polymeric layer comprising a polymer selected from the group consisting of copolymers and terpolymers of N-vinyl pyrrolidone, said copolymers being of N-vinyl pyrrolidone and an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms, said terpolymers being of N-vinyl pyrrolidone, an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms and a lower alkyl ester of an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms.

2. A photosensitive element as defined in claim 1 wherein the mole fraction of N-vinyl pyrrolidone monomer in the initial monomer mixture used to produce said copolymers and terpolymers is at least 0.5.

3. A photosensitive element as defined in claim 1 wherein said polymer layer comprises a copolymer and the mole fraction of N-vinyl pyrrolidone monomer in the initial monomer mixture used to produce said copolymer is about 0.9.

4. A photosensitive element as defined in claim 1 wherein said polymeric layer comprises a terpolymer and the mole fractions of N-vinyl pyrrolidone, the α,β-unsaturated aliphatic monocarboxylic acid and the lower alkyl ester of an α,β-unsaturated aliphatic monocarboxylic acid in the initial monomer mixture used to produce said terpolymers are about 0.64, 0.11 and 0.25, respectively.

5. A photosensitive element as defined in claim 1 wherein said color-providing material is a dye developer.

6. A photosensitive element comprising a plurality of photosensitive silver halide emulsions, each of said emulsions being selectively sensitized to different portions of the spectrum, a dye developer associated with each of said emulsions, said dye developer being a compound which contains in the same molecule both the chromophoric system of a dye and also a silver halide developing function, at least one of said dye developers being disposed in a polymeric layer contiguous with the emulsion with which it is associated, said polymeric layer comprising a polymer selected from the group consisting of copolymers and terpolymers of N-vinyl pyrrolidone, said copolymers being of N-vinyl pyrrolidone and an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms, said terpolymers being of N-vinyl pyrrolidone, an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms and a lower alkyl ester of an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms.

7. A photosensitive element as defined in claim 6 wherein the mole fraction of N-vinyl pyrrolidone monomer in the initial monomer mixture used to produce said copolymers and terpolymers is at least 0.5.

8. A photosensitive element as defined in claim 6 wherein said polymeric layer comprises a copolymer and the mole fraction of N-vinyl pyrrolidone monomer in the initial monomer mixture used to produce said copolymer is about 0.9.

9. A photosensitive element as defined in claim 6 wherein said polymeric layer comprises a terpolymer and the mole fractions of N-vinyl pyrrolidone, the α,β-unsaturated aliphatic monocarboxylic acid and the lower alkyl ester of an α,β-unsaturated aliphatic monocarboxylic acid in the inital monomer mixture, used to produce said terpolymer are about 0.64, 0.11 and 0.25, respectively.

10. In a process of forming a photographic image in color wherein a latent image contained in an exposed silver halide emulsion layer of a photosensitive element is developed to provide an imagewise distribution of color-providing materials selected from the group consisting of dyes and dye intermediates in said emulsion, and said imagewise distribution of color-providing materials is transferred by an aqueous alkaline processing solution to a superposed image-receiving layer to impart to said image-receiving layer a colored image, the improvement of having the color-providing materials in a polymeric layer which is contiguous with and behind the silver halide emulsion layer and, during processing, permeating said photosensitive element with said aqueous alkaline processing solution and solubilizing said color-providing materials from said polymeric layer, said polymeric layer comprising a polymer selected from the group consisting of copolymers and terpolymers of N-vinyl pyrrolidone, said copolymers being of N-vinyl pyrrolidone and an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms, said terpolymers being of N-vinyl pyrrolidone, an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms and a lower alkyl ester of an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms.

11. A process as defined in claim 10 wherein the mole fraction of N-vinyl pyrrolidone monomer in the initial monomer mixture used to produce said copolymers and said terpolymers is at least 0.5.

12. A process as defined in claim 10 wherein said polymeric layer comprises a copolymer and the mole fraction of N-vinyl pyrrolidone monomer in the initial monomer mixture used to produce said copolymers is about 0.9.

13. A process as defined in claim 10 wherein said polymeric layer comprises a terpolymer and the mole fractions of N-vinyl pyrrolidone, the α,β-unsaturated aliphatic monocarboxylic acid and the lower alkyl ester of an α,β-unsaturated aliphatic monocarboxylic acid in the initial monomer mixture used to produce said terpolymer are about 0.64, 0.11 and 0.25 respectively.

14. In a process of forming transfer images in color which comprises exposing a photosensitive element including a silver halide emulsion layer and a polymeric layer, said polymeric layer containing a dye developer, said dye developer being a compound which contains within the same molecule a chromophoric system of a dye and also a silver halide developing function, permeating said photosensitive element with an aqueous alkaline processing solution and solubilizing at least a portion of said dye developer from said polymeric layer, developing the latent image in the exposed emulsion in the presence of said dye developer whereby said dye developer is immobilized in exposed areas but is mobile in unexposed areas in said emulsion, thereby providing an imagewise distribution of mobile dye developer, and transferring at least a portion of said mobile dye developer to a superposed image-receiving layer to form a positive image, the improvement

of having the dye developer in a polymeric layer of a polymer selected from the group consisting of copolymers and terpolymers of N-vinyl pyrrolidone, said copolymer being of N-vinyl pyrrolidone and an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms, said terpolymers being of N-vinyl pyrrolidone, an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms and a lower alkyl ester of an α,β-unsaturated aliphatic monocarboxylic acid containing less than six carbon atoms.

15. A process as defined in claim 14 wherein the mole fraction of N-vinyl pyrrolidone monomer in the initial monomer mixture used to produce said copolymers and terpolymers is at least 0.5.

16. A process as defined in claim 14 wherein said polymeric layer comprises a copolymer and the mole fraction of N-vinyl pyrrolidone monomer in the initial monomer mixture used to produce said copolymer is about 0.9.

17. A process as defined in claim 14 wherein said polymeric layer comprises a terpolymer and the mole fractions of N-vinyl pyrrolidone, the α,β-unsaturated aliphatic monocarboxylic acid and the lower alkyl ester of an α,β-unsaturated aliphatic monocarboxylic acid in the initial monomer mixture used to produce said terpolymer are approximately 0.64, 0.11 and 0.25, respectively.

18. A process as defined in claim 14 wherein said polymeric layer is placed behind the silver halide emulsion layer.

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