

[54] **MORDANT VEHICLE FOR COLOR
IMAGE TRANSFER RECEIVERS**

[75] Inventor: **Thomas I. Abbott**, Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company**,
Rochester, N.Y.

[22] Filed: **Aug. 24, 1971**

[21] Appl. No.: **174,545**

[52] U.S. Cl.....**96/29 D, 96/3, 96/57,**
96/77, 96/84 A

[51] Int. Cl.....**G03c 5/54, G03c 5/58**

[58] Field of Search.....**96/84 A, 57, 3, 29 D, 77**

[56] **References Cited**

UNITED STATES PATENTS

3,625,694 12/1971 Cohen et al.96/84

Primary Examiner—J. Travis Brown
Assistant Examiner—Alfonso T. Suro Pico
Attorney—Robert W. Hampton et al.

[57] **ABSTRACT**

The use of a hydrophobic, alkali-permeable polymer as a binder for a dye mordant in a dye image-receiving layer employed in color diffusion transfer systems results in less stain than conventional gelatin vehicles.

23 Claims, No Drawings

MORDANT VEHICLE FOR COLOR IMAGE TRANSFER RECEIVERS

This invention relates to the art of photography and more particularly to color diffusion transfer film units, reception elements and methods for obtaining stable, positive, right-reading diffusion transfer dye images of high quality.

U.S. Pat. No. 3,227,550 of Whitmore and Mader issued Jan. 4, 1966 and U.S. Pat. No. 3,227,552 of Whitmore issued Jan. 4, 1966 describe photographic image transfer processes wherein an immobile coupler is reacted with oxidized color developer to form a mobile dye which is transferred by diffusion to a receiving layer to form a color image. During the development phase of the color development diffusion transfer process, the image dyes formed in the respective blue, green and red-sensitive silver halide emulsion layers diffuse into an image-receiving layer of the receiving element where the dyes are mordanted to form the transferred image. At the same time, small amounts of development reaction products and unused color developer diffuse into the image-receiving layer. When the receiving element is separated from the photosensitive element, oxygen in the atmosphere causes rapid oxidation of the unused developer; self-coupling of the developer occurs, thereby producing a yellowish-brown stain, particularly in the highlight or minimum density areas. It would be desirable to reduce the stain.

U.S. Pat. No. 3,445,228 issued May 20, 1969, of Beavers et al. discloses that a white pigment contained in an interlayer of a dye image-receiving element for use in the above-described process helps to conceal the stain formed in an acid layer and functions also as a timing layer. It would be desirable to provide an image-receiving element wherein the staining propensities of the image-receiving layer are decreased.

U.S. Pat. Nos. 3,271,147; 3,271,148 and 3,312,549 describe various dye image-receiving layers for use in color diffusion transfer systems. The vehicles for dispersing the dye mordant are hydrophilic binders such as gelatin and various water-soluble cellulose derivatives.

It is an object of this invention to provide a film unit employing an image-receiving element capable of receiving stable dye images of high quality.

It is another object of this invention to provide a process for producing a transfer image wherein the receiving element does not require a post-processing washing step.

It is another object of this invention to provide an image-receiving element wherein the staining propensities of the dye image-receiving layer are decreased.

It is another object of this invention to provide a process of forming a transfer image employing a novel dye image-receiving element.

These and other objects are achieved by a photographic film unit according to my invention, which is adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members, such as would be found in a camera designed for in-camera processing, comprising:

- a. a photosensitive element comprising a support having thereon at least one, and preferably three, photosensitive silver halide emulsion layers, each silver halide emulsion layer having associated

therewith a dye image-providing material comprising a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible dye;

- b. a dye image-receiving layer comprising a dye mordant dispersed in a hydrophobic, alkali-permeable binder; and

- c. a rupturable container containing an alkaline processing composition and which is adapted to be positioned during processing of the film unit so that a compressive force applied to the container by pressure-applying members in a camera will effect a discharge of the container's contents within the film unit;

the film unit containing an aromatic, primary amino color developing agent, preferably in the rupturable container.

The polymers used in accordance with my invention to disperse the dye mordant have a tendency to reduce the amount of unwanted development reaction products and unused color developer which normally accompany diffusible dye images formed by reacting an initially nondiffusible coupler with an oxidized, aromatic primary amino color developing agent. As mentioned above, unwanted development reaction products and unused color developers on a dye image-receiving layer are objectionable because of the tendency of these materials to form stain, particularly in the highlight or Dmin. areas.

Dye mordants normally employed in color diffusion transfer systems are usually dispersed in hydrophilic colloids as described previously. Many of these dye image-receiving layers are designed for post-washing of the print to remove undesirable products. However, when left unwashed, the Dmin in such prints increases rapidly.

Use of a hydrophobic, alkali-permeable polymer as the binder for the dye mordant in accordance with my invention provides a relatively thin, hydrophobic element which can be produced from a non-aqueous medium. Since such mordant layers are much thinner than a gelatin mordant layer and because the element is water-impermeable yet alkali solution-permeable, unwanted development reaction products and unused color developer pick-up are held to a minimum without affecting dye imbibition. The elements also have improved physical properties such as repellency to the viscous processing composition, low curl, better gloss and improved dye stability.

Any polymer can be employed as the binder for the dye mordant in accordance with my invention as long as it is hydrophobic and alkali-permeable. Such polymers include ethyl cellulose which is especially preferred, polyvinyl acetal, or copolymers comprising recurring units of acrylic acid, acrylamide, sulfoalkyl acrylate, sulfoalkyl methacrylate, alkyl acrylate, alkyl methacrylate, etc. The remaining units of the copolymers can be derived from other ethylenically unsaturated monomers well known to those skilled in the art. Such copolymers are described, for example, in U.S. Pat. No. 3,411,911 of Dykstra issued Nov. 19, 1968; U.S. Pat. No. 3,411,912 of Dykstra et al. issued Nov. 19, 1968; U.S. Pat. No. 3,488,708 of Smith issued Jan. 6, 1970; and U.S. Pat. No. 3,220,844 of Houck et al. issued Nov. 30, 1965.

The amount of hydrophobic, alkali-permeable polymer to be used as the vehicle for the dye mordant can be varied widely depending upon the imaging-chemistry employed, the particular dye mordant used, etc. Generally, the dye image-receiving layer will be from about 0.04 to about 0.25 mil in thickness.

My invention can be used not only in diffusion transfer systems wherein the image-receiving element is located on a separate support from the photosensitive element, but also in diffusion transfer systems wherein the image-receiving element is integral with the photosensitive element.

In one embodiment of my invention wherein the image-receiving element is separate from the photosensitive element, the novel dye image-receiving element comprises a support having thereon a dye image-receiving layer comprising a dye mordant dispersed in a hydrophobic, alkali-permeable polymer.

A pH-lowering material layer and a timing layer, described hereinafter, can also be employed in the dye image-receiving element to increase the stability of the transferred image. Although not required, a light-reflective layer comprising a white pigment in a binder, described hereinafter, can also be employed in the dye image-receiving element, if desired. The light-reflective layer can be located underneath the dye image-receiving layer or can be combined with a timing layer if one is employed.

The above-described dye image-receiving element of the film unit is adapted to be superposed on the photosensitive element after exposure thereof. The development and transfer operations can be effected by bathing either or both the exposed photosensitive element and the dye image-receiving element in a developing solution before rolling into contact with each other, or a viscous developing composition can be placed between the elements for spreading in a predetermined amount across and into contact with the exposed surface of the photosensitive elements. The viscous developing composition is desirably utilized in one or more pods attached to the reception sheet or photosensitive element that can be readily ruptured when development is desired as described, for example, in U.S. Pat. Nos. 2,559,643; 2,647,049; 2,661,293; 2,698,244; 2,698,798; and 2,774,668.

During the development phase of a color diffusion transfer process according to my invention, the dye image-providing material formed in the respective blue-, green- and red-sensitive silver halide emulsion layers diffuse out of the photosensitive element through the viscous developer composition and into the dye image-receiving layer, e.g., into the dye image-receiving element described above, where the dyes are mordanted to form the transferred image.

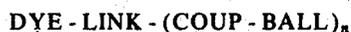
In another embodiment of my invention, the dye image-receiving layer is located integral with the photosensitive element between the support and the lowermost photosensitive silver halide emulsion layer. Such integral receiver-negative photosensitive elements are described in copending U.S. application Ser. No. 115,459 of Barr, Bush and Thomas filed Feb. 16, 1971 and now abandoned. In such an embodiment, the support for the photosensitive element is transparent and is coated with the dye image-receiving layer, a substantially opaque, light-reflective layer, e.g., TiO_2 , and

the various layers forming the color-forming units. After exposure of the photosensitive element, a rupturable container containing an alkaline processing composition and an opaque process sheet are brought into super-posed position. Pressure-applying members in a camera rupture the container and spread processing composition over the photosensitive element as the film unit is withdrawn from the camera. The processing composition develops the exposed silver halide layers and dye images are formed as a function of development which diffuse to the image-receiving layer to provide a positive, right-reading image which is viewed through the transparent support on the opaque reflecting layer background. For further details concerning this particular integral film unit, its preparation and use, reference is made to the above-mentioned U.S. application Ser. No. 115,459 of Barr, Bush and Thomas filed Feb. 16, 1971.

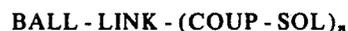
Another embodiment of integral receiver-negative photosensitive systems in which my invention can be employed is described in U.S. Ser. No. 115,552 of Cole filed Feb. 16, 1971 and now abandoned. In such an embodiment, the support for the color diffusion transfer system is transparent and is coated with the image-receiving layer, a substantially opaque, light-reflective layer, e.g., TiO_2 , and then the various layers forming the color-forming units and a top transparent sheet. A rupturable container containing an alkaline processing composition and an opacifier is positioned adjacent to the top layer and sheet. The film unit is placed in camera, exposed through the top transparent sheet and then passed between a pair of pressure-applying members in the camera as it is being removed therefrom. The pressure-applying members rupture the container and spread processing composition and opacifier over the negative portion of the film unit to render it light-insensitive. The processing composition develops the exposed silver halide layers and dye images are formed as a result of development which diffuse to the image-receiving layer to provide a positive, right-reading image which is viewed through the transparent support on the opaque reflecting layer background. For further details concerning this particular integral film unit, its preparation and use, reference is made to the above-mentioned Cole U.S. application Ser. No. 115,552 filed Feb. 16, 1971.

In the photographic film units according to my invention, there is associated with each silver halide emulsion layer in the photosensitive element a dye image-providing material comprising a nondiffusible coupler which produces a diffusible dye on reaction with oxidized aromatic primary amino color developing agent in an alkaline processing composition.

The nondiffusible couplers employed in this invention include those having the formulas:



and



wherein

1. DYE is a radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing radical;

2. LINK is a connecting radical such as an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical or an azoxy radical;
3. COUP is a coupler radical such as a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, COUP being substituted in the coupling position with LINK;
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render such coupler nondiffusible during development in the alkaline processing composition;
5. SOL is a hydrogen atom or an acidic solubilizing group when the color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when the color developing agent is free of an acidic solubilizing group; and
6. n is an integer of 1 to 2 when LINK is an alkylidene radical, and n is 1 when LINK is an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical or an azoxy radical.

For further details concerning the above-described couplers, their preparation and use, reference is made to U.S. Pat. No. 3,227,550 of Whitmore et al. issued Jan. 4, 1966; U.S. Pat. No. 3,227,552 of Whitmore issued Jan. 4, 1966; and British Pat. No. 904,364, page 19, lines 1-41.

The film assembly of my invention can be used to produce positive images in single or multicolors. In a three-color system, each silver halide emulsion layer of the film assembly of my invention will have associated therewith a dye image-providing material possessing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion, i.e., the blue-sensitive silver halide emulsion layer will have a yellow dye image-providing material associated therewith, the green-sensitive silver halide emulsion layer will have a magenta dye image-providing material associated therewith, and the red-sensitive silver halide emulsion layer will have a cyan dye image-providing material associated therewith. The dye image-providing material associated with each silver halide emulsion layer can be contained either in the silver halide emulsion layer itself or in a layer contiguous to the silver halide emulsion layer.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light sensitive silver halide emulsion of the multilayer photographic elements of the invention. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye may be added in the form of a dispersion as described in Owens et al. British Pat. No. 1,154,781 issued June 11, 1969. For optimum results the dye can either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al. U.S. Pat. No. 2,526,632, issued Oct. 24, 1950; Sprague U.S. Pat. No. 2,503,776, issued Apr. 11, 1950; Brooker et al. U.S. Pat. No. 2,493,748, issued Jan. 10, 1950; and Taber et al. U.S. Pat. No. 3,384,486 issued May 21, 1968. Spectral sensitizers which can be used include

the cyanines, merocyanines, complex (tri or tetranuclear) merocyanines, complex (tri or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g. enamine hemicyanines), oxonols and hemioxonols. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain. The merocyanine dyes can contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoins, rhodanines, oxazolinediones, thiazolinediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition, super-sensitizing addenda which do not absorb visible light can be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S. Pat. No. 2,933,390 issued Apr. 19, 1960 and Jones et al. U.S. Pat. No. 2,937,089 issued May 17, 1960.

The various silver halide emulsion layers of a color film assembly of the invention can be disposed in the usual order, i.e., the blue-sensitive silver halide emulsion layer first with respect to the exposure side, followed by the green-sensitive and red-sensitive silver halide emulsion layers. If desired, a yellow dye layer or a Carey Lea silver layer can be present between the blue-sensitive and green-sensitive silver halide emulsion layer for absorbing or filtering blue blue radiation that may be transmitted through the blue-sensitive layer. If desired, the selectively sensitized silver halide emulsion layers can be disposed in a different order, e.g., the blue-sensitive layer first with respect to the exposure side, followed by the red-sensitive and green-sensitive layers.

The silver halide emulsions used in this invention can comprise, for example, silver chloride, silver bromide, silver chlorobromide, silver bromiodide, silver chlorobromiodide or mixtures thereof. The emulsions can be coarse or fine grain and can be prepared by any of the well-known procedures, e.g., single jet emulsions such as those described in Trivelli and Smith *The Photographic Journal*, Vol. LXXIX, May, 1939 (pp 330-338), double jet emulsions, such as Lippman emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. No. 2,222,264 issued Nov. 19, 1940; Illingsworth U.S. Pat. No. 3,320,069 issued May 16, 1967; and McBride U.S. Pat. No. 3,271,157 issued Sept. 6, 1966. Surface image emulsions can be used or internal image emulsions can be used such as those described in Davey et al U.S. Pat. No. 2,592,250 issued May 8, 1952; Porter et al. U.S. Pat. No. 3,206,313 issued Sept. 14, 1965; Berriman U.S. Pat. No. 3,367,778 issued Feb. 6, 1968; and Bacon et al. U.S. Pat. No.

3,447,927 issued June 3, 1969. The emulsions may be regular grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, Vol. 12, No. 5, Sept./Oct., 1964, (pp. 242-251). Negative type emulsions may be used or direct positive emulsions may be used such as those described in Leermakers U.S. Pat. No. 2,184,013 issued Dec. 19, 1939; Kendall et al. U.S. Patent No. 2,541,472 issued Feb. 13, 1951; Berriman U.S. Pat. No. 3,367,778 issued Feb. 6, 1968; Schouwenaars British Pat. No. 723,019 issued Feb. 2, 1955; Illingsworth et al. French Pat. No. 1,520,821 issued Mar. 4, 1968; Illingsworth U.S. Pat. No. 3,501,307 issued Mar. 17, 1970; Ives U.S. Pat. No. 2,563,785 issued Aug. 7, 1951; Knott et al. U.S. Pat. No. 2,456,953 issued Dec. 21, 1948; and Land U.S. Pat. No. 2,861,885 issued Nov. 25, 1958.

The emulsions used with this invention may be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. No. 1,623,499 issued Apr. 5, 1927; Waller et al. U.S. Pat. No. 2,399,083 issued Apr. 23, 1946; McVeigh U.S. Pat. No. 3,297,447 issued Jan. 10, 1967; and Dunn U.S. Pat. No. 3,297,446 issued Jan. 10, 1967.

The silver halide emulsions used with this invention may contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959; Dann et al. U.S. Pat. No. 3,046,134 issued July 24, 1962; Carroll et al. U.S. Pat. No. 2,944,900 issued July 12, 1960; and Goffe U.S. Pat. No. 3,294,540 issued Dec. 27, 1966.

The silver halide emulsions used in the practice of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al. U.S. Pat. No. 2,131,038 issued Sept. 27, 1938; and Allen et al. U.S. Pat. No. 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959; and Heimbach et al. U.S. Pat. No. 2,444,605 issued July 6, 1948; the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135 issued Nov. 22, 1966; the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652 issued Feb. 22, 1966; the oximes described in Carroll et al. British Pat. No. 623,448 issued May 18, 1949; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927 issued July 16, 1946; Kennard et al. U.S. Pat. No. 3,266,897 issued Aug. 16, 1966; and Luckey et al. U.S. Pat. No. 3,397,987 issued Aug. 20, 1968; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263 issued Aug. 28, 1951; and Yutzy et al. U.S. Pat. No. 2,597,915 issued May 27, 1952; and the tetrazoles described in Hoppe U.S. Pat. No. 3,352,672 issued Nov. 14, 1967.

If the silver halide emulsion employed with the non-diffusible couplers described above is a direct positive silver halide emulsion, such as an internal image emulsion or a solarizing emulsion, which is developable in unexposed areas, a positive image can be obtained on the dye image-receiving layer. In this embodiment, the nondiffusible coupler can be located in the silver halide emulsion itself. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the exposed photosensitive silver halide emulsion layers. The aromatic primary amino color developing agent present in the film unit develops each of the silver halide emulsion layers in the unexposed areas (since the silver halide emulsions are direct positive ones), thus causing the developing agent to become oxidized imagewise corresponding to the unexposed areas of the direct positive silver halide emulsion layers. The oxidized developing agent then reacts with the nondiffusible coupler present in each silver halide emulsion layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of the imagewise exposure of each of the silver halide emulsion layers. At least a portion of the imagewise distributions of diffusible cyan, magenta and yellow dye diffuse to the image-receiving layer to provide a positive dye image upon separation of the receiver from the negative.

Internal image silver halide emulsions useful in the above-described embodiment are direct positive emulsions that form latent images predominantly inside the silver halide grains, as distinguished from silver halide grains that form latent images predominantly on the surface thereof. Such internal image emulsions were described by Davey et al. in U.S. Pat. No. 2,592,250 issued Apr. 8, 1952, and elsewhere in the literature. These emulsions can also contain fogging or nucleating agents such as those described in U.S. Pat. Nos. 2,588,982; 2,563,785; 3,227,552; etc.

As previously mentioned, the aromatic primary amino color developing agent employed in the above-described embodiment is preferably present in the alkaline processing composition in the rupturable pod. The color developing agent can also be incorporated into the negative portion of the film unit as a separate layer, e.g., by employing a Schiff base derivative of an aromatic primary amino color developing agent such as that formed by reacting o-sulfobenzaldehyde and N,N-diethyl-3-methyl-4-aminoaniline. Such incorporated developing agent will be activated by the alkaline processing composition. While the incorporated developing agent can be positioned in any layer of the photosensitive element from which it can be readily made available for development upon activation with alkaline processing composition it is generally either incorporated in the light-sensitive silver halide emulsion layers or in layers contiguous thereto. As mentioned above, aromatic primary amino color developing agents employed in certain embodiments of this invention are preferably p-phenylenediamine developing agents. These developing agents are well known to those skilled in the art and include the following compounds and salts thereof:

- 4-amino-N,N-diethyl-3-methyl aniline,
- N,N-diethyl-p-phenylenediamine,
- N-ethyl- β -methane-sulfonamido-ethyl-3-methyl-4-amino aniline,

4-amino-N-ethyl-3-methyl-N-(β -sulfoethyl)aniline,
 4-amino-N-ethyl-3-methoxy-N-(β -sulfoethyl)aniline,
 4-amino-N-ethyl-N-(β -hydroxyethyl)aniline,
 4-amino-N,N-diethyl-3-hydroxymethyl aniline,
 4-amino-N-methyl-N-(β -carboxyethyl)aniline,
 4-amino-N,N-bis(β -hydroxyethyl)aniline,
 4-amino-N,N-bis(β -hydroxyethyl)-3-methyl aniline,
 3-acetamido-4-amino-N,N-bis(β -hydrox-
 yethyl)aniline,
 4-amino-N-ethyl-N-(2,3-dihydroxypropyl)-3-methyl
 aniline,
 4-amino-N,N-diethyl-3-(3-hydroxypropoxy)aniline,
 and the like.

In a color film unit according to the invention, each
 silver halide emulsion layer containing a dye image-
 providing material or having the dye image-providing
 material present in a contiguous layer may be separated
 from the other silver halide emulsion layers in the nega-
 tive portion of the film unit by materials in addition to
 those described above, including gelatin, calcium al-
 ginate, or any of those disclosed in U.S. Pat. No.
 3,384,483, polymeric materials such as polyvinyla-
 mides ad disclosed in U.S. Pat. No. 3,421,892, or any of
 those disclosed in U.S. Pat. Nos. 2,992,104; 3,043,692;
 3,044,873; 3,061,428; 3,069,263; 3,069,264;
 3,121,011 and 3,427,158.

Generally speaking, except where noted otherwise,
 the silver halide emulsion layers in the invention com-
 prise photosensitive silver halide dispersed in gelatin
 and are about 0.6 to 6 microns in thickness; the dye
 image-providing materials are dispersed in an aqueous
 alkaline solution-permeable polymeric binder, such as
 gelatin, as a separate layer about 1 to 7 microns in
 thickness, and the alkaline solution-permeable
 polymeric interlayers, e.g., gelatin, are about 1 to 5
 microns in thickness. Of course these thicknesses are
 approximate only and can be modified according to the
 product desired. In addition to gelatin, other suitable
 hydrophilic materials which can be employed include
 both naturally-occurring substances such as proteins,
 e.g., gelatin derivatives, cellulose derivatives,
 polysaccharides such as dextran, gum arabic and the
 like; and synthetic polymeric substances such as water
 soluble polyvinyl compounds like poly(vinylpyr-
 rolidone), acrylamide polymers and the like.

The photographic emulsion layers and other layers of
 a photographic element employed in the practice of
 this invention can also contain alone or in combination
 with hydrophilic, water-permeable colloids, other
 synthetic polymeric compounds such as dispersed vinyl
 compounds such as in latex form and particularly those
 which increase the dimensional stability of the photo-
 graphic materials. Suitable synthetic polymers include
 those described for example, in Nottorf U.S. Pat. No.
 3,142,568 issued July 28, 1964; White U.S. Pat. No.
 3,193,386 issued July 6, 1965; Houck et al. U.S. Pat.
 No. 3,062,674 issued Nov. 6, 1962; Houck et al. U.S.
 Pat. No. 3,220,844 issued Nov. 30, 1965; Ream et al.
 U.S. Pat. No. 3,287,289 issued Nov. 22, 1966; and
 Dykstra U.S. Pat. No. 3,411,911 issued Nov. 19, 1968.
 Particularly effective are those water-soluble polymers
 of alkyl acrylates and methacrylates, acrylic acid, sul-
 foalkyl acrylates or methacrylates, those which have
 cross-linking sites which facilitate hardening or curing
 described in Smith U.S. Pat. No. 3,488,708 issued Jan.
 6, 1970, and those having recurring sulfobetaine units
 as described in Dykstra Canadian Pat. No. 774,054.

Any material can be employed as the dye mordant in
 this invention as long as the desired function of mor-
 danting or otherwise fixing the dye images will be ob-
 tained. The particular material chosen will, of course,
 depend upon the dye to be mordanted. If acid dyes are
 to be mordanted, the image-receiving layer can contain
 basic polymeric mordants such as polymers of amino
 guanidine derivatives of vinyl methyl ketone such as
 described in Minsk U.S. Pat. No. 2,882,156 issued Apr.
 14, 1959, and basic polymeric mordants such as
 described in copending U.S. Application Ser. No.
 100,491 of Cohen et al. filed Dec. 21, 1970. Other
 mordants useful in my invention include poly-4-vinyl-
 pyridine, the 2-vinyl pyridine polymer metho-p-toluene
 sulfonate and similar compounds described in Sprague
 et al. U.S. Pat. No. 2,484,430 issued Oct. 11, 1949, and
 cetyl trimethylammonium bromide, etc. Effective dye
 mordants are also described in Whitmore U.S. Pat. No.
 3,271,148 and Bush U.S. Pat. No. 3,271,147, both is-
 sued Sept. 6, 1966.

The image-receiving layer can also contain ultra-
 violet absorbing materials to protect the mordanted
 dye images from fading due to ultraviolet light,
 brightening agents such as the stilbenes, coumarins,
 triazines, oxazoles, dye stabilizers such as the
 chromanols, alkylphenols, etc.

Use of a pH-lowering material associated with the
 dye image-receiving element of the invention will
 usually increase the stability of the transferred image.
 Generally, the pH-lowering material will effect a reduc-
 tion in the pH of the image layer from about 13 or 14 to
 at least 11 and preferably 5-8 within a short time after
 imbibition. For example, polymeric acids as disclosed
 in U.S. Pat. No. 3,362,819 or solid acids or metallic
 salts, e.g., zinc acetate, zinc sulfate, magnesium
 acetate, etc., as disclosed in U.S. Pat. No. 2,584,030
 may be employed with good results. Such pH-lowering
 materials reduce the pH of the film unit after develop-
 ment to terminate development and substantially
 reduce further dye transfer and thus stabilize the dye
 image. The pH-lowering material can be present as a
 separate layer between the dye image-receiving layer
 and its support where the receiver is a separate element
 or between the dye image-receiving layer and the
 lowermost silver halide emulsion layer in an integral
 receiver-negative element.

An inert timing or spacer layer can be employed in
 the practice of my invention over the pH-lowering layer
 which "times" or controls the pH reduction as a func-
 tion of the rate at which alkali diffuses through the inert
 spacer layer. Examples of such timing layers include
 gelatin, polyvinyl alcohol or any of those disclosed in
 U.S. Pat. No. 3,455,686. The timing layer is also effec-
 tive in evening out the various reaction rates over a
 wide range of temperatures, e.g., premature pH reduc-
 tion is prevented when imbibition is effected at tem-
 peratures above room temperature, for example, at 95°
 to 100°F. The timing layer is usually about 0.1 to about
 0.7 mil in thickness and may contain a light reflective
 material, such as titanium dioxide, if desired. Especially
 good results are obtained when the timing layer com-
 prises a hydrolyzable polymer or a mixture of such
 polymers which are slowly hydrolyzed by the
 processing composition. Examples of such hydrolyza-
 ble polymers include polyvinyl acetate, polyamides,
 cellulose esters, etc.

The alkaline processing composition employed in this invention is the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 12, and preferably containing a developing agent as described previously. The solution also preferably contains a viscosity-increasing compound such as a high-molecular-weight polymer, e.g., a water-soluble ether inert to alkaline solutions such as hydroxyethyl cellulose or alkali metal salts of carboxymethyl cellulose such as sodium carboxymethyl cellulose. A concentration of viscosity-increasing compound of about 1 to about 5 percent by weight of the processing composition is preferred which will impart thereto a viscosity of about 100 cps. to about 200,000 cps.

While the alkaline processing composition used in this invention can be employed in a rupturable container, as described previously, other methods of applying processing composition could be employed, e.g., bathing the photosensitive element in a processing bath, interjecting processing composition with communicating members similar to hypodermic syringes which are attached either to a camera or camera cartridge, etc.

While the film units of my invention can be modified so as to be employed in roll form, they are preferably used in cartridges similar to those described in U.S. Pat. Nos. 3,080,805; 3,161,118; and 3,161,122; said patents also illustrating typical cameras for performing color diffusion transfer processes of my invention.

The supports for the photographic elements of this invention can be any material as long as it does not deleteriously effect the photographic properties of the film unit and is dimensionally stable. Typical flexible sheet materials include cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film poly(ethylene-terephthalate) film, polycarbonate film, poly- α -olefins such as polyethylene and polypropylene film, and related films or resinous materials as well as glass, paper, metal, etc. The support is usually about 2 to 6 mils in thickness.

While the invention has been described with reference to layers of silver halide emulsions and dye image-providing materials, dotwise coating, such as would be obtained using a gravure printing technique, could also be employed. In this technique, small dots of blue, green and red-sensitive emulsions have associated therewith, respectively, dots of yellow, magenta and cyan color-providing substances. After development, the transferred dyes would tend to fuse together into a continuous tone.

The photographic layers employed in the practice of this invention may contain surfactants such as saponin; anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. No. 2,600,831 issued June 17, 1952; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 3,133,816 issued May 19, 1964; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Pat. No. 1,022,878 issued March 16, 1966; and Knox U.S. Pat. No. 3,514,293 issued May 26, 1970.

The various layers, including the photographic layers, employed in the practice of this invention can

contain light absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. No. 3,253,921 issued May 31, 1966; Gaspar U.S. Pat. No. 2,274,782 issued Mar. 3, 1942; Silberstein et al. U.S. Pat. No. 2,527,583 issued Oct. 31, 1950; and VanCampen U.S. Pat. No. 2,956,879 issued Oct. 18, 1960.

The sensitizing dyes and other addenda used in the practice of this invention can be added from water solutions or suitable organic solvent solutions may be used. The compounds can be added during various procedures including those described in Collins et al. U.S. Pat. No. 2,912,343 issued Nov. 10, 1959; McCrossen et al. U.S. Pat. No. 3,342,605 issued Sept. 19, 1967; Audran U.S. Pat. No. 2,966,287 issued Aug. 15, 1961 and Johnson et al. U.S. Pat. No. 3,425,835 issued Feb. 4, 1969.

The photographic layers used in the practice of this invention may be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin U.S. Pat. No. 2,681,294 issued June 15, 1954. If desired, two or more layers may be coated simultaneously by the procedure described in Russell U.S. Pat. No. 2,761,791 issued Sept. 4, 1956; Hughes U.S. Pat. No. 3,508,947 issued Apr. 28, 1970; and Wynn British Pat. No. 837,095 issued June 9, 1960. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat. No. 968,453 issued Sept. 2, 1964 and Lu-Valle et al. U.S. Pat. No. 3,219,451 issued Nov. 23, 1965.

The photographic and other hardenable layers used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes as described in Allen et al. U.S. Pat. No. 3,232,764 issued Feb. 1, 1966; ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers as described in Burness et al. U.S. Pat. No. 3,539,644 issued Nov. 10, 1970; active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodi-imides, polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

The following example further illustrates the invention.

EXAMPLE

Dye image-receiving elements are prepared by coating the following mordant compositions on a polyethylene-coated paper support:

Composition A		
Gelatin (10% aqueous solution)		75.0 g
Triethylpropylammonium chloride		4.5 g
Distilled water to		500.0 g
Composition B		
Ethyl cellulose (5% toluene solution)		425.0 g
Triethylpropylammonium chloride		20.0 g
Toluene to		500.0 g

The compositions are coated such that the dried coating from Composition A contains 250 milligrams gelatin and 150 milligrams mordant and the dried coating from Composition B contains about 160 milligrams ethyl cellulose and 160 milligrams mordant per square foot of support.

A multicolor photographic element of the type described in Example 1 of Whitmore et al. U.S. Pat. No. 3,227,550 issued Jan. 9, 1966, is prepared. The emulsions are direct positive, gelatino, silver bromiodide emulsions containing cyan, magenta and yellow dye-forming couplers in the red, green and blue light-recording emulsions, respectively.

Samples of the above photosensitive element are exposed to a multicolor test object. The following processing composition is spread from a pod between the exposed surface of the elements and the superposed image-receiving elements by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers:

benzyl alcohol	10.0 ml.
sodium hydroxide	25.0 g.
4-amino-N-ethyl-N-β-hydroxyethyl aniline	20.0 g.
5-nitrobenzimidazole	0.24 g.
hydroxyethyl cellulose	30.0 g.
Water to	1 liter

After 60 seconds at about 24°C, the dye image-receiving elements are peeled apart from the negative. After several weeks keeping under room light conditions, the minimum densities are obtained as follows:

Mordant Composition	D min		
	Red	Green	Blue
A (control)	1.04	1.32	1.81
B	0.50	0.52	0.95

The above results indicate the significant improvement in D min, which is attributable to less stain, which is obtained in the use of the dye image-receiving element according to my invention.

The invention has been described with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. In a photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

- a. a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer, each said silver halide emulsion layer having associated therewith a non-diffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible dye;
- b. a dye image-receiving layer comprising a dye mordant dispersed in a binder; and
- c. a rupturable container containing an alkaline processing composition and which is adapted to be positioned during processing of said film unit so that a compressive force applied to said container by said pressure-applying members will effect a discharge of the container's contents within said film unit;

said film unit containing an aromatic primary amino color developing agent; the improvement comprising employing a hydrophobic, alkali-permeable polymer as said binder.

2. The photographic film unit of claim 1 wherein said photosensitive element comprises a support having thereon a red-sensitive silver halide emulsion layer hav-

ing associated therewith a cyan dye image-providing material comprising a non-diffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye, a green-sensitive silver halide emulsion layer having associated therewith a magenta dye image-providing material comprising a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye, and a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye image-providing material comprising a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye.

3. The film unit of claim 1 wherein said dye image-receiving layer is located in said photosensitive element between said support and the lowermost photosensitive silver halide emulsion layer.

4. The film unit of claim 1 wherein said dye image-receiving layer is coated on a separate support and is adapted to be superposed on said photosensitive element after exposure thereof.

5. The film unit of claim 4 wherein said rupturable container is so positioned during processing of said film unit that a compressive force applied to said container by said pressure-applying members will effect a discharge of the container's contents between said dye image-receiving layer and the outermost layer of said photosensitive element.

6. The film unit of claim 1 which also contains a pH-lowering material.

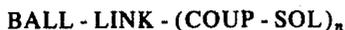
7. The film unit of claim 1 wherein said hydrophobic, alkali-permeable polymer is ethyl cellulose, polyvinyl acetal, or a copolymer comprising units of acrylic acid, acrylamide, sulfoalkyl acrylate, sulfoalkyl methacrylate, alkyl acrylate or alkyl methacrylate.

8. The film unit of claim 1 wherein said polymer is ethyl cellulose.

9. In a photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

1. a photosensitive element comprising a support having thereon the following layers in sequence:
 - a. a direct-positive, red-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye;
 - b. an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent;
 - c. a direct-positive, green-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;
 - d. an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent; and
 - e. a direct-positive, blue-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to

produce a diffusible yellow dye; each said non-diffusible coupler having the formula:



wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
 2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;
 3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;
 4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
 5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and
 6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;
 - II. a dye image-receiving element comprising a support having thereon a dye mordant dispersed in a binder, said element being adapted to be superposed over said blue-sensitive silver halide emulsion layer after exposure of said photosensitive element; and
 - III. a rupturable container containing an alkaline processing composition and which is adapted to be positioned during processing of said film unit so that a compressive force applied to said container by said pressure-applying members will effect a discharge of the container's contents between said dye image-receiving layer and said blue-sensitive silver halide emulsion layer of said photosensitive element;
- said film unit containing an aromatic primary amino color developing agent; the improvement comprising employing a hydrophobic, alkali-permeable polymer as said binder.
10. The film unit of claim 9 wherein said hydrophobic, alkali-permeable polymer is ethyl cellulose, polyvinyl acetal, or a copolymer comprising units of acrylic acid, acrylamide, sulfoalkyl acrylate, sulfoalkyl methacrylate, alkyl acrylate or alkyl methacrylate.
 11. The film unit of claim 9 wherein said polymer is ethyl cellulose.
 12. A reception element comprising a support having thereon a dye image-receiving layer comprising a dye mordant dispersed in a hydrophobic, alkali-permeable polymer.

13. The reception element of claim 12 wherein said polymer is ethyl cellulose, polyvinyl acetal, or a copolymer comprising units of acrylic acid, acrylamide, sulfoalkyl acrylate, sulfoalkyl methacrylate, alkyl acrylate or alkyl methacrylate.

14. The reception element of claim 12 wherein said polymer is ethyl cellulose.

15. The reception element of claim 12 which includes a pH-lowering layer between said support and said dye image-receiving layer.

16. The reception element of claim 15 wherein said pH-lowering layer comprises a polymeric acid.

17. The reception element of claim 16 wherein a timing layer is present between said polymeric acid layer and said dye image-receiving layer.

18. The reception element of claim 17 wherein said hydrophobic, alkali-permeable polymer is ethyl cellulose, polyvinyl acetal, or a copolymer comprising units of acrylic acid, acrylamide, sulfoalkyl acrylate, sulfoalkyl methacrylate, alkyl acrylate or alkyl methacrylate.

19. The reception element of claim 17 wherein said hydrophobic, alkali-permeable polymer is ethyl cellulose.

20. In a process of forming a transfer image comprising:

- a. imagewise-exposing a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer, each said silver halide emulsion layer having associated therewith a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible dye;
- b. treating the layer outermost from the support of said exposed photosensitive element with an alkaline processing composition to effect development of each of said exposed silver halide emulsion layers;
- c. forming an imagewise distribution of diffusible dye image-providing material as a function of said imagewise exposure of each said silver halide layer; and
- d. at least a portion of each said imagewise distribution of diffusible dye image-providing material diffusing to a dye image-receiving layer comprising a dye mordant dispersed in a binder;

the improvement comprising employing as said binder a hydrophobic, alkali-permeable polymer.

21. The process of claim 20 wherein said treatment step (b) is effected by

- A. superposing over the layer outermost from the support of said photosensitive element said dye image-receiving layer coated on a support;
- B. positioning a rupturable container containing said alkaline processing composition between said exposed photosensitive element and said dye image-receiving layer; and
- C. applying a compressive force to said container to effect a discharge of the container's contents between said outermost layer of said exposed photosensitive element and said dye image-receiving layer.

22. The process of claim 21 wherein said polymer is ethyl cellulose, polyvinyl acetal, or a copolymer comprising units of acrylic acid, acrylamide, sulfoalkyl acrylate, sulfoalkyl methacrylate, alkyl acrylate or alkyl methacrylate.

23. The process of claim 21 wherein said polymer is ethyl cellulose.

* * * * *

5

10

15

20

25

30

35

40

45

50

55

60

65