

[54] **DIFFUSION TRANSFER RECEPTION
ELEMENTS, FILM UNITS AND
PROCESSES THEREFOR**

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

[21] Appl. No.: **174,506**

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

[51] Int. Cl. **G03c 7/00, G03c 5/54, G03c 5/48**

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

[56] **References Cited**

UNITED STATES PATENTS

3,635,707 1/1972 Cole 96/3

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[57] **ABSTRACT**

A dye image-receiving element comprising a light-reflecting layer underneath a dye image-receiving layer, each of the layers containing a basic polymeric mordant, is useful in color development diffusion transfer systems utilizing immobile couplers which form diffusible dyes.

30 Claims, No Drawings

DIFFUSION TRANSFER RECEPTION ELEMENTS, FILM UNITS AND PROCESSES THEREFOR

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.

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 conceals 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 higher maximum dye densities and lower minimum dye densities are obtainable, as well as a reduction of visible stain and background densities.

Accordingly, 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 employing a novel image-receiving element.

It is another object of this invention to provide an image-receiving element providing higher maximum dye densities of the transferred image, as well as lower minimum dye densities, both initially and after subjecting to various atmospheric conditions for extended periods of time.

It is another object of this invention to provide a film unit employing an image-receiving element more resistant to oxidized color developer stain, thereby reducing the minimum or background densities.

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 pri-

mary amino color developing agent to produce a diffusible dye;

b. a dye image-receiving element comprising a support having thereon (1) a light-reflecting layer comprising a basic polymeric mordant and an opacifying agent and (2) a dye image-receiving layer comprising a basic polymeric mordant; and

c. a rupturable container containing an alkaline processing composition and which is adapted to be positioned between said photosensitive element and said dye image-receiving element during processing of said 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 between the image-receiving element and the outermost layer of the photosensitive element; the film unit containing an aromatic, primary amino color developing agent, preferably in the rupturable container.

The dye image-receiving layer of my film unit is located on a separate support which is adapted to be superposed on the photosensitive element after exposure thereof. Upon rupturing the pod, the processing composition diffuses through the film unit thereby initiating imagewise development of the silver halide emulsion layers. Dye images formed as a result of the reaction of oxidized developer with nondiffusible couplers contained in each silver halide emulsion layer or in a layer contiguous thereto are formed as a function of the imagewise exposure of each said silver halide emulsion layer. At least a portion of the imagewise distributions of diffusible dye diffuses to the image-receiving layer. A positive dye image is viewable upon separation of the image-receiving element from the negative element.

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 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 thiohydantoin, rhodanines, oxazolidenediones, thiazolidenediones, 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, supersensitizing 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 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 bromoiodide, silver chlorobromoiodide 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 Lippmann 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. Pat. 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 mercaptotetraazoles 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.

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

DYE-LINK-(COUP-BALL)_n and BALL-LINK-(COUP-SOL)_n wherein:

1 DYE is a dye 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.

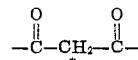
The acidic solubilizing radicals attached to the diffusible dye-producing couplers described above can be solubilizing radicals which, when attached to the coupler or developer moieties of the dyes, render the dyes diffusible in alkaline processing compositions. Typical of such radicals are carboxylic, sulfonic, ionizable sulfonamide and hydroxy-substituted groups that lend to dyes negative charges.

The nature of the ballast groups in the diffusible dye-producing coupler compounds described above (BALL-) is not critical as long as they confer nondiffusibility to the coupler compounds. Typical ballast groups include long-chain alkyl radicals linked directly or indirectly to the coupler molecules, as well as aromatic radicals of the benzene and naphthalene series, etc., linked directly or indirectly to the coupler molecules by a splittable linkage, or by a removable or irremovable but otherwise nonfunctional linkage depending upon the nature of the coupler compound. Useful ballast groups have at least 8 carbon atoms.

Typical dye radical substituents (DYE-) include azo, azomethine, indoaniline, indophenol, anthraquinone and related dye radicals well-known in the art that exhibit selective absorption in the visible spectrum. The dye radicals contain acidic solubilizing moieties.

With regard to the above-described coupler radicals (COUP-), the "coupling position" is well-known to those skilled in the photographic art. The 5-pyrazolone coupler radicals couple at the carbon atom in the 4-

position, the phenolic coupler radicals, including α -naphthols, couple at the carbon atom in the 4-position, and the open-chain ketomethylene coupler radicals couple to the carbon atom forming the methylene moiety (e.g.,



*denoting the coupling position). Pyrazolotriazole couplers and their coupling position are described, for example, in U.S. Pat. No. 3,061,432 and U.S. Application Ser. No. 778,329 of Bailey et al. filed Nov. 22, 1968 and now abandoned.

Particularly good results are obtained when the cyan-producing coupler has the formula BALL-O-CYANCOUP, the magenta-producing coupler has the formula BALL-N=N-MAGCOUP and the yellow-producing coupler has the formula BALL-O-YELLCOUP wherein:

a. BALL is a photographically inert organic ballasting radical having at least eight carbon atoms and of such molecular size and configuration as to render the coupler nondiffusible during development in an alkaline processing composition;

b. CYANCOUP is a phenolic coupler radical substituted in the 2-position with a fully substituted amido group and attached to the -O-moiety of the cyan-producing coupler in the coupling position;

c. MAGCOUP is a 5-pyrazolone coupler radical joined to the -N=N- moiety of the magenta-producing coupler in the coupling position; and

d. YELLCOUP is an open-chain ketomethylene coupler radical attached to the -O- moiety of the yellow-producing coupler in the coupling position.

The term "nondiffusing" used herein, as applied to the couplers, has the meaning commonly applied to the term in color photography and denotes materials which for all practical purposes do not migrate or wander through organic colloid layers, such as gelatin, comprising the sensitive elements of the invention. The same meaning is to be attached to the term "immobile."

The term "diffusible" as applied to the dyes formed from the "nondiffusing" couplers in this invention has the converse meaning and denotes materials having the property of diffusing effectively through the colloid layers of the sensitive elements in the presence of the "nondiffusing" materials from which they are derived. "Mobile" has the same meaning.

When the couplers having the formula DYE-LINK-(COUP-BALL)_n as described above are reacted with oxidized color developing agent, the connecting radical (LINK) is split and a diffusible preformed dye (DYE) is released which diffuses imagewise to a reception layer. An acidic solubilizing group on the preformed dye lends diffusibility to the dye molecule. The coupling portion of the coupler (COUP) couples with the color developing agent oxidation product to form a dye that is nondiffusible because of the attacked ballasting group (BALL) in a noncoupling position. In this type of coupler, the color of the diffusible dye is determined by the color of the preformed dye moiety (DYE), the color of the reaction product of color developer oxidation product and the coupler moiety (COUP) being unimportant to the color of the diffusible image.

When couplers having the formula BALL-LINK-(COUP-SOL)_n, as described above are reacted with oxidized color developing agent, the connecting radical (LINK) is split and a diffusible dye is formed with the color developing agent oxidation product and the coupling portion (COUP) of the coupler which diffuses imagewise to a reception layer. Diffusibility is imparted to the dye by an acidic solubilizing group attached to a noncoupling position of the coupling portion (COUP) of the coupler or to the color developing agent. The ballasting portion of the coupler remains immobile. In this type of coupler, the color of the diffusible dye is determined by the color of the reaction product of color developer oxidation product and the coupler moiety (COUP).

In using both types of couplers in the invention, the production of diffusible dye images is a function of the reduction of developable silver halide images which may involve direct or reversal development of the silver halide emulsions with an aromatic primary amino developing agent. If the silver halide emulsion employed 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 in 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. Specific examples of such nondiffusing couplers and other details concerning this type of photographic chemistry are found in U.S. Pat. Nos. 3,227,550 and 3,227,552.

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. Internal-image silver halide emulsions can be defined in terms of the increased maximum density obtained when developed with "internal-type" developers over that obtained when developed with "surface-type" developers. Suitable internal-image emulsions are those which, when measured according to normal photographic techniques by coating a test portion of

the silver halide emulsion on a transport support, exposing to a light-intensity scale having a fixed time between 0.01 and 1 second, and developing for 3 minutes at 20° C. in Developer A below ("internal-type" developer), have a maximum density at least five times the maximum density obtained when an equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in Developer B described below ("surface-type" developer). Preferably, the maximum density in Developer A is at least 0.5 density unit greater than the maximum density in Developer B.

Developer A

hydroquinone	15 g.
monomethyl-p-aminophenol sulfate	15 g.
sodium sulfite (desiccated)	50 g.
potassium bromide	10 g.
sodium hydroxide	25 g.
sodium thiosulfate	20 g.
water to make 1 liter	

Developer B

p-hydroxyphenylglycine	10 g.
sodium carbonate	100 g.
water to make 1 liter	

The solarizing direct-positive silver halide emulsions useful in the above-described embodiment are well-known silver halide emulsions which have been effectively fogged either chemically or by radiation to a point which corresponds approximately to the maximum density of the reversal curve as shown by Mees, *The Theory of the Photographic Process*, published by the MacMillan Co., New York, N.Y., 1942, pages 261-297. Typical methods for the preparation of solarizing emulsions are shown by Groves, British Pat. No. 443,245 published Feb. 25, 1936, who subjected emulsions to Roentgen rays "until an emulsion layer formed therefrom, when developed without preliminary exposure, is blackened up to the apex of its graduation curve;" Szaz, British Pat. No. 462,730 published Mar. 15, 1937, the use of either light or chemicals such as silver nitrate, organic sulfur compounds and dyes to convert ordinary silver halide emulsions to solarizing direct-positive emulsions; and Arens, U.S. Pat. No. 2,005,837 issued June 25, 1935, the use of silver nitrate and other compounds in conjunction with heat to effect solarization. Kendall and Hill, U.S. Pat. NO. 2,541,472 issued Feb. 13, 1951, show useful solarized emulsions particularly susceptible to exposure with long wavelength light and initial development to produce the Herschel effect described by Mees above, produced by adding benzothiazoles and other compounds to the emulsions which are fogged either chemically or with white light. In using the emulsions, a sufficient reversal image exposure is employed using minus blue light of from about 500-700 mμ wave length, preferably 520-554 mμ, to destroy substantially the latent image in the silver halide grains in the region of the image exposure. Particularly useful are the fogged direct-positive emulsions of Berriman, U.S. Pat. No. 3,367,778; Illingsworth, U.S. Pat. Nos. 3,501,305, 3,501,306 and 3,501,307; and combinations thereof.

Internal-image silver halide emulsions which contain or which are processed in the presence of fogging or

nucleating agents are particularly useful in the above-described embodiment employing nondiffusible couplers, since the use of fogging agents is a convenient way to inject electrons into the silver halide grains. Suitable fogging agents include the hydrazines disclosed in Ives, U.S. Pat. Nos. 2,588,982 issued Mar. 11, 1952, and 2,563,785 issued Aug. 7, 1951; the hydrazides and hydrazones disclosed in Whitmore, U.S. Pat. No. 3,227,552 issued Jan. 4, 1966; hydrazone quaternary salts described in Lincoln and Heseltine, U.S. Ser. No. 828,064 filed Apr. 28, 1969 and now abandoned; or mixtures thereof. The quantity of fogging agent employed can be widely varied depending upon the results desired. Generally, the concentration of fogging agent is from about 1 to about 20 mg. per square foot of photosensitive layer in the photosensitive element or from about 0.1 to about 2 g. per liter of developer if it is located in the developer.

Other embodiments of my invention employ the photosensitive elements described in the above-mentioned U.S. Pat. Nos. 3,227,550, 3,227,551 and 3,227,552 and in British Pat. No. 904,364, page 19, lines 1-41. These embodiments all employ the nondiffusible couplers described above.

In the above-described embodiments employing nondiffusible couplers, interlayers are generally employed between the various photosensitive color-forming units to scavenge oxidized developing agent and prevent it from forming an unwanted dye in another color-forming unit. Such interlayers would generally comprise a hydrophilic polymer such as gelatin and an immobilizing coupler, which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product.

As previously mentioned, the aromatic primary amino color developing agent employed in the above-described embodiments 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 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 -methanesulfonamidoethyl-3-methyl-4-aminoaniline, 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 -hydrox-

ethyl)aniline, 4-amino-N,N-bis(β -hydroxyethyl)-3-methyl aniline, 3-acetamido-4-amino-N,N-bis(β -hydroxyethyl)aniline, 4-amino-N-ethyl-N-(2,3-dihydroxypropyl)-3-methyl aniline, 4-amino-N,N-diethyl-3-(3-hydroxypropoxy)aniline, and the like.

The rupturable container employed in this invention can be of the type disclosed in U.S. Pat. Nos. 2,543,181, 2,634,886, 2,653,732, 2,723,051, 3,056,492, 3,056,491 and 3,152,515. In general, such containers comprise a rectangular sheet of fluid and air-impervious material folded longitudinally upon itself to form two walls which are sealed to one another along their longitudinal and end margins to form a cavity in which the processing composition is contained.

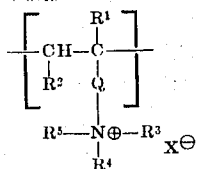
In a color film unit according to the invention, each silver halide emulsion layer containing a dye image-providing material or having the dye image-providing material present in a contiguous layer may be separated from the other silver halide emulsion layers in the negative portion of the film unit by materials in addition to those described above, including gelatin, calcium alginate, or any of those disclosed in U.S. Pat. No. 3,384,483, polymeric materials such as polyvinylamides as 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 comprise photosensitive silver halide dispersed in gelatin and are about 0.6 to 6 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 include both naturally occurring substances such as proteins, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like, and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

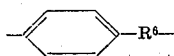
The photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain, alone or in combination with hydrophilic, water-permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic 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 water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl 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.

As described above, the dye image-receiving layer and the polymer in the light-reflecting layer in this invention comprises a basic polymeric mordant. Especially preferred basic polymeric mordants are those described and claimed in copending U.S. Ser. No. 709,812 filed Mar. 1, 1968, now abandoned, of my co-workers Cohen, King and Minsk and their continuation-in-part applications, U.S. Ser. Nos. 100,487 and 100,491 filed Dec. 21, 1970 of which continuation-in-part application the last one, U.S. Serial No. 100,491 is now abandoned. The basic polymeric mordants are composed of a polymer having quaternary nitrogen groups and at least two aromatic nuclei for each quaternary nitrogen atom, said monomer: compound being substantially free of carboxy groups. In addition, the basic polymeric mordants described in Cohen et al, U.S. Pat. No. 3,488,706 issued Jan. 6, 1970, can also be employed with good results.

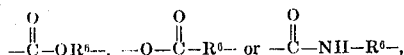
Preferred basic polymeric mordants comprise units of the following formula in copolymerized relationship with units of at least one other ethylenically unsaturated monomer:



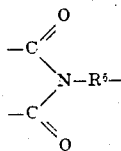
wherein R^1 and R^2 can each be hydrogen atoms, lower alkyl, e.g., one to six carbon atoms such as methyl, ethyl, propyl, n-butyl, t-butyl, and the like; and R^2 can additionally be a group containing at least one aromatic nucleus including substituted aryl, e.g., phenyl, naphthyl, tolyl, etc.; Q can be a covalent bond, a divalent alkylene, arylene, aralkylene or arylenealkyl radical such as:



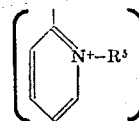
or other radicals including:



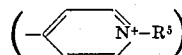
where $\text{---}\text{R}^6\text{---}$ is an alkylene radical typically having one to four carbon atoms or R^2 can be taken together with Q to form a



group; R^3 , R^4 and R^5 are lower alkyl including substituted alkyl, e.g., aralkyl, cyanomethyl, alkoxyethyl, carboalkoxy-methyl, carbamoylmethyl, etc.; aryl, including substituted aryl, e.g., phenyl, naphthyl, tolyl, etc.; or R^3 and R^4 and the nitrogen atom to which they are attached can be taken together to represent the atoms and covalent bonds necessary to form a quaternized nitrogen-containing heterocyclic ring which is attached to Q such as a 2-pyridinium



or 4-pyridinium



ring; and X^- is an anion, i.e., a monovalent negative salt-forming radical or atom in ionic relationship with the positive salt-forming radical or polymer cation such as a halide, alkyl, sulfate, sulfonate, for example, such as p-toluenesulfonate, dialkyl phosphate and the like; wherein said polymer is substantially free of carboxy groups. Preferably, the positive salt-forming radical of said polymer comprises at least two aromatic nuclei for each quaternary nitrogen atom in said polymer.

The above-described basic polymeric mordants are water-soluble polymers having a polyhydrocarbon backbone and are composed of recurring units supplying quaternized nitrogen atoms and preferably having at least two aromatic nuclei, such as aryl groups, per quaternized nitrogen atom. The polymers should be substantially free of carboxy groups for the presence of carboxy groups in the interpolymers interferes with effective dye mordanting.

The above-described basic polymeric mordants are generally prepared by quaternizing an intermediate polymer having tertiary nitrogen atoms with an alkylating or aralkylation agent. The method of preparation of the intermediate polymer containing the tertiary nitrogen atoms for subsequent quaternization is not critical. Any of the methods known in the art such as mass, solution, or bead polymerization, as well as condensation polymerization, can be used, and the catalysts known to the art such as ultraviolet light, peroxides, azo compounds, e.g., azobisisobutyronitrile, etc., can be employed.

The mordanting amount of basic polymeric mordant to be employed in a dye image-receiving layer will vary over a wide range depending upon the amount of dye to be mordanted, the particular polymer employed, the imaging chemistry involved, etc. This amount can easily be determined by one skilled in the art.

Typical ethylenically unsaturated monomers which can be used to form ethenic interpolymers comprising the above-described basic polymeric mordants include ethylene, propylene, 1-butene, isobutene, 2-methylpentene, 2-methylbutene, 1,1,4,4-tetramethylbutadiene, styrene, alpha-methylstyrene; monoethylenically unsaturated esters of aliphatic acids such as vinyl acetate, isopropenyl acetate, allyl acetate, etc.; esters of ethylenically unsaturated mono- or dicarboxylic acids such as methyl acrylate, methyl methacrylate, ethyl acrylate, diethyl methylene malonate, etc.; monoethylenically unsaturated compounds such as acrylonitrile, allyl cyanide, and dienes such as butadiene and isoprene.

For further details concerning the above-described basic polymeric mordants and their preparation, reference is made to the above-mentioned U.S. Pat. No. 3,488,706 and U.S. Ser. No. 709,812 filed Mar. 1, 1968, of Cohen, King and Minsk and the continuation-in-part applications Ser. Nos. 100,487 and 100,491 filed Dec. 21, 1970.

Basic polymeric mordants included within the scope of the invention include the following:

copoly[styrene--N,N-dimethyl-N-ethoxycarbonylmethyl-N-(3-maleimidopropyl)ammonium chloride];
 copoly[styrene--N,N-dimethyl-N-cyanomethyl-N-(3-maleimidopropyl)ammonium chloride];
 copoly[styrene--N,N-dimethyl-N-methoxymethyl-N-(3-maleimidopropyl)ammonium chloride];
 copoly[styrene--N,N,N-trimethyl-N-(3-maleimidopropyl)-ammonium p-toluenesulfonate];
 copoly[styrene--N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride];
 copoly[styrene--N-(3-acrylamidopropyl)-N,N-dimethyl-N-4-nitrobenzylammonium chloride];
 copoly[styrene--N-(3-acrylamidopropyl)-N,N-dimethyl-N-(1-naphthylmethyl)ammonium chloride];
 copoly[styrene--N-(3-acrylamidopropyl)-N-benzyl-N,N-dimethylammonium chloride];
 copoly[styrene--N-(3-maleimidopropyl)-N,N-dimethyl-N-(4-phenylbenzyl)ammonium chloride];
 copoly[styrene--N-(2-methacryloyloxyethyl)-N,N-dimethyl-N-benzylammonium chloride];
 copoly(styrene--1-benzyl-2-methyl-5-vinylpyridinium chloride);
 copoly[2-vinylpyridine--2-vinyl-N-(1-naphthylmethyl)-pyridinium chloride];
 copoly[N-acrylamidopropyl-N,N-dimethyl-N-vinylloxycarbomethylammonium chloride--N-benzyl-N,N-dimethyl-N-vinylloxycarbomethylammonium chloride];
 copoly[2-vinylnaphthalene--N-(1-naphthylmethyl)-N,N-dimethyl-N-maleimidopropylammonium chloride]; and
 copoly[styrene--N-(3-acrylamidopropyl)-N-carbamoylmethyl-N,N-dimethylammonium chloride].

Use of a pH-lowering layer in the dye image-receiving element employed in this invention will increase the stability of the transferred image. Generally, the pH-lowering layer will effect a reduction 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 may be employed. Such polymeric acids reduce the pH of the film unit after development to further terminate dye transfer and thus stabilize the dye image. Such polymeric acids comprise polymers containing acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium or potassium, or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide. The polymers can also contain potentially acid-yielding groups such as anhydrides or lactones or other groups which are capable of reacting with bases to capture and retain them. Generally, the most useful polymeric acids contain free carboxyl groups, being insoluble in water in the free acid form and which form water-soluble sodium and/or potassium salts. Examples of such polymeric acids include dibasic acid half-ester derivatives of cellulose, which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with orthosulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose;

polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo-substituted aldehydes, e.g., o-, m- or p- benzaldehyde sulfonic acid or carboxylic acid; ethylene/maleic anhydride copolymers and their partial esters; methylvinyl ether/maleic anhydride copolymers and their partial esters such as the butyl half-ester of medium viscosity poly-(methylvinyl ether/maleic anhydride); etc. In addition, solid monomeric acid materials could also be used such as palmitic acid, oxalic acid, sebacic acid, hydrocinnamic acid, metanilic acid, paratoluenesulfonic acid and benzenedisulfonic acid. Other suitable materials are disclosed in U.S. Pat. Nos. 3,422,075 and 2,635,048. The pH-lowering layer is usually about 0.3 to about 1.5 mils in thickness and is preferably located in the dye image-receiving element between the support and the opacifying layer.

The light-reflecting layer employed in my invention comprises a basic polymeric mordant, such as the ones described above, and an opacifying agent. Particularly desirable are white opacifying agents since they would provide an esthetically pleasing background on which to view a transferred dye image and would possess the optical properties desired for reflection of incident radiation. Suitable opacifying agents include titanium dioxide, barium sulfate, zinc oxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, or mixtures thereof in widely varying amounts depending upon the degree of opacity desired. Especially good results are obtained with titanium dioxide. Zinc oxide in combination with titanium dioxide may also be employed to great advantage as disclosed and claimed in copending application U.S. Ser. No. 174,443 of my co-workers Abbott, Dappen and Irani filed of even date herewith. Brightening agents such as the stilbenes, coumarins, triazines and oxazoles can also be added to the light-reflecting or opacifying layer, if desired. It is believed that any stain resulting from excess developing agent or oxidized developing agent is hidden in or masked by this layer.

Where a pH-lowering layer is employed, such as a polymeric acid layer, the basic polymeric mordant in the light-reflecting layer will function as a "timing" layer and will control the pH reduction of the dye image-receiving element as a function of the rate at which the alkali diffuses through the layer. Of course, widely varying amounts of the basic polymeric mordant can be employed in the light-reflecting layer, depending upon the results desired.

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. 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 solution 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 con-

tainer, as described previously, other methods of applying processing composition could also 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 affect the photographic properties of the film unit and is dimensionally stable. Typical materials include cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethyleneterephthalate) 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.

The dye image-receiving element of my invention can be prepared by employing various leveling agents and/or coating aids such as the copolymers of dimethyl siloxane and polyoxyalkylene ether described in U.S. Pat. Nos. 3,324,058 and 3,483,240. The dye image-receiving element according to my invention can also be overcoated with a hydrophilic colloid layer such as gelatin, gum arabic or any of those materials described in U.S. Application Ser. No. 100,486 of Abbott, filed Dec. 21, 1970. In addition, the dye image-receiving element of my invention can contain ultraviolet absorbing materials to protect the mordanted dye images from fading due to ultraviolet light. Such materials are described in U.S. Pat. Nos. 3,460,942; 3,069,262; 3,330,680 and 3,330,656.

The photographic layers employed in the practice of this invention may contain surfactants such as saponin or any of the materials described in U.S. Pat. Nos. 2,600,831; 3,133,816; or 3,514,293 or British Pat. No. 1,022,878.

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 solvents 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. 2,996,287 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. 2,681,294 issued June

15, 1954. If desired, two or more layers may be coated simultaneously by the procedures 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 LuValle 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, carbodiimides, polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

The following examples further illustrate the invention.

EXAMPLE 1:

A. A control dye image-receiving element is prepared by coating the following layers in the order recited on a polyethylene-coated paper support;

1. polymeric acid layer of poly(methyl vinyl ether/maleic anhydride) (825 mg./ft.²);
2. mordant layer of copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride] (750 mg./ft.²); and
3. overcoat of gelatin (36 mg./ft.²).

B. A dye image-receiving element according to my invention is prepared by coating the following layers in the order recited on a polyethylene-coated paper support:

1. polymeric acid layer of poly(methyl vinyl ether/maleic anhydride) (825 mg./ft.²);
2. light-reflecting layer of copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride] (400 mg./ft.²) and titanium dioxide (1000 mg./ft.²);
3. mordant layer of copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride] (350 mg./ft.²); and
4. overcoat layer of gelatin (36 mg./ft.²).

A multicolor photographic element of the type described in Example 1 of Whitmore et al., U.S. Pat. No. 3,227,550 issued Jan. 4, 1966, is prepared. The emulsions are directpositive, gelatino, silver bromide 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:

potassium hydroxide	35.0 g.
4-amino-N-ethyl-N- β -hydroxyethyl aniline	40.0 g.
5-methylbenzimidazole	0.05 g.

hydroxyethyl cellulose
water to 1 liter

30.0 g.

After 60 seconds at about 20° C., the dye image-receiving element is pulled apart from the negative. The minimum densities to red, green and blue are then measured, both fresh and after 4 days at 140° F./70 per cent relative humidity. The following results are obtained:

Receiver	Dmin (Fresh)			Dmin (4 Days 140° F./70% R.H.)		
	Red	Green	Blue	Red	Green	Blue
A (control)	0.36	0.27	0.27	0.46	0.41	0.47
B	0.30	0.28	0.31	0.30	0.28	0.29

2. light-reflecting layer of titanium dioxide (1000 mg./ft.²) and the compound identified in the table below;

3. mordant layer of copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride] (200 mg./ft.²) and gelatin (200 mg./ft.²); and

4. overcoat layer of gelatin (36 mg./ft.²).

The above dye image-receiving elements are then tested according to the same procedure described in Example 1. The minimum and maximum densities to red, green and blue are then measured, both fresh and after 7 days at 140° F./70% R.H. The following results are obtained:

Polymer in opacifying layer (mg./ft. ²)	Fresh						7 Days at 140° F./70% R.H.					
	Dmin.			Dmax.			Dmin.			Dmax.		
	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue
Polyvinyl alcohol (400)	.20	.20	.20	1.59	1.51	1.61	.25	.27	.30	1.10	1.23	0.66
Polyvinyl alcohol (800)	.20	.20	.20	1.74	1.61	1.62	.32	.34	.36	1.39	1.46	0.83
Gelatin (400)	.35	.43	.31	1.53	2.01	1.61	.39	.45	.31	1.10	1.63	0.71
Copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride] (400)	.23	.23	.23	1.98	1.80	1.88	.29	.27	.30	1.74	1.63	0.94

The results indicate the enhanced Dmin keeping stability which is obtained in accordance with my invention.

EXAMPLE 2:

C. A control element is prepared similar to (A) in Example 1 except that the mordant layer (2) contains 200 mg./ft.² instead of 750 mg./ft.² of the mordant compound and also contains 200 mg./ft.² of gelatin. Layer (3) is also omitted.

D. an image-receiving element similar to (B) of Example 1 is prepared except that mordant layer (3) contains 200 mg./ft.² instead of 350 mg./ft.² of the mordant compound and also contains 200 mg./ft.² of gelatin. Layer (4) is also omitted.

The above dye image-receiving elements are then tested according to the same procedure described in Example 1. The minimum and maximum densities to red, green and blue are then measured, both fresh and after 4 days at 140° F./70% R.H. The following results are obtained:

Receiver	Fresh						4 days at 140° F./70% R.H.		
	Dmin.			Dmax.			Dmin.		
	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue
C (control)	.30	.27	.24	1.81	1.85	1.67	.37	.44	.50
D	.30	.28	.27	2.30	2.20	2.12	.30	.20	.26

The above results indicate the increase in Dmax obtainable according to the invention, as well as the enhanced Dmin keeping stability.

Example 3:

Dye image-receiving elements are prepared by coating the following layers in the order recited on a polyethylene-coated paper support:

1. polymeric acid layer of poly(methyl vinyl ether/maleic anhydride) (825 mg./ft.²);

The above results illustrate the increase in Dmax which is obtained in accordance with the invention (the last one on the table), as well as the enhanced Dmax and Dmin keeping stability.

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 nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible dye;

b. a dye image-receiving layer coated on a support

and adapted to be superposed on said photosensitive element after exposure thereof; and

c. a rupturable container containing an alkaline processing composition and which is adapted to be positioned between said photosensitive element and said dye image-receiving layer 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 the outermost layer of said photosensitive element and said dye image-receiving layer;

said film unit containing an aromatic primary amino color developing agent; the improvement comprising employing a basic polymeric mordant as said dye image-receiving layer, said dye image-receiving layer being coated over a light-reflecting layer comprising a basic polymeric mordant and an opacifying agent.

2. The photographic film unit of claim 1 wherein said photosensitive element comprises a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a cyan dye image-providing material comprising a nondiffusible 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.

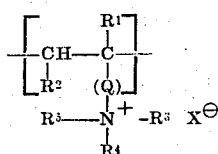
3. The photographic film unit of claim 1 including a pH-lowering layer between said light-reflecting layer and its support.

4. The photographic film unit of claim 3 wherein said pH-lowering layer comprises a polymeric acid.

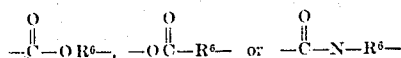
5. The photographic film unit of claim 1 wherein said opacifying agent comprises titanium dioxide.

6. The photographic film unit of claim 4 wherein said opacifying agent comprises titanium dioxide.

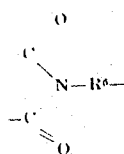
7. The photographic film unit of claim 1 wherein each said basic polymeric mordant comprises a polymer having at least 1/3 of the units represented by the following formula in copolymerized relationship with units of at least one other ethylenically unsaturated monomer.



wherein R^1 and R^2 are hydrogen atoms or lower alkyl groups and R^2 can additionally be a group containing at least one aromatic nucleus; Q can be a covalent bond, a divalent alkylene radical, a divalent atylene radical, a divalent aralkylene radical, a divalent arylenalkylene radical,



wherein R^6 is an alkylene radical, or R^2 can be taken together with Q to form a



group; R^3 , R^4 and R^5 can be lower alkyl or aryl groups, or R^3 and R^4 and the nitrogen atom to which they are attached can be taken together to represent the atoms and bonds necessary to form a quaternized nitrogen-containing heterocyclic ring which is attached to Q, and X^- is a monovalent negative salt-forming radical or atom; wherein said polymer is substantially free of carboxy groups.

8. The photographic film unit of claim 7 wherein each said basic polymeric mordant is copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride].

9. The photographic film unit of claim 6 wherein each said basic polymeric mordant comprises copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride].

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

I. 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 nondiffusible coupler having the formula: $\text{DYE-LINK-(COUP-BALL)}_n$ or $\text{BALL-LINK-(COUP-SOL)}_n$ 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 nondif-

fusible 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

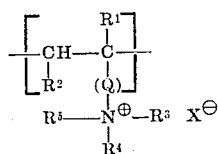
6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;

II. a dye image-receiving element comprising a support having thereon a dye image-receiving layer, said element being adapted to be superposed over said blue-sensitive silver halide emulsion layer after exposure of said photosensitive element; and

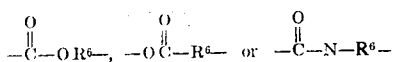
III. a rupturable container containing an alkaline processing composition and which is adapted to be positioned during processing of said film unit so that a compressive force applied to said container by said pressure-applying members will effect a discharge of the container's contents between said dye image-receiving layer and said blue-sensitive silver halide emulsion layer of said photosensitive element;

said film containing an aromatic primary amino color developing agent; the improvement comprising employing as said dye image-receiving element a support having thereon a polymeric acidic material layer, a light-reflecting layer comprising a basic polymeric mordant and an opacifying agent, and a dye image-receiving layer comprising a basic polymeric mordant.

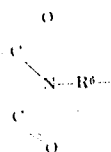
11. The photographic film unit of claim 10 wherein each said basic polymeric mordant comprises a polymer having at least one-third of the units represented by the following formula in copolymerized relationship with units of at least one other ethylenically unsaturated monomer:



wherein R^1 and R^2 are hydrogen atoms or lower alkyl groups and R^2 can additionally be a group containing at least one aromatic nucleus; Q can be a covalent bond, a divalent alkylene radical, a divalent arylene radical, a divalent aralkylene radical, a divalent arylenealkylene radical,



wherein R^6 is an alkylene radical, or R^2 can be taken together with Q to form a



group; R^3 , R^4 and R^5 can be lower alkyl or aryl groups, or R^3 and R^4 and the nitrogen atom to which they are attached can be taken together to represent the atoms and bonds necessary to form a quaternized nitrogen-containing heterocyclic ring which is attached to Q, and $\text{X}^{\ominus}$ is a monovalent negative salt-forming radical or atom; wherein said polymer is substantially free of carboxy groups and wherein the positive salt-forming radical of said polymer comprises at least two aryl groups for each quaternary nitrogen atom in said polymer and said opacifying agent comprises titanium dioxide.

12. 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. superposing over the layer outermost from the support of said exposed photosensitive element a dye image-receiving layer coated on a support;

- c. positioning a rupturable container containing an alkaline processing composition comprising an aromatic primary amino color developing agent between said exposed photosensitive element and said dye image-receiving layer;

- d. 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;

- e. forming an imagewise distribution of diffusible dye image-providing material as a function of said image-wise exposure of each said silver halide emulsion layer; and

- f. at least a portion of each said imagewise distribution of diffusible dye image-providing material diffusing to said dye image-receiving layer;

the improvement comprising employing a basic polymeric mordant as said dye image-receiving layer, said dye image-receiving layer being coated over a light-reflecting layer comprising a basic polymeric mordant and an opacifying agent.

13. The process of claim 12 wherein said photosensitive element comprises a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a cyan dye image-providing material comprising a nondiffusible 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.

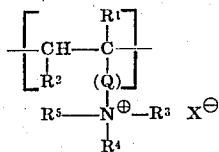
14. The process of claim 12 including a pH-lowering layer between said light-reflecting layer and its support.

15. The process of claim 14 wherein said pH-lowering layer comprises a polymeric acid.

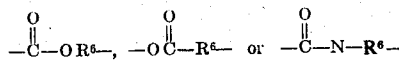
16. The process of claim 12 wherein said opacifying agent comprises titanium dioxide.

17. The process of claim 15 wherein said opacifying agent comprises titanium dioxide.

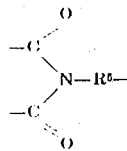
18. The process of claim 12 wherein each said basic polymeric mordant comprises a polymer having at least one-third of the units represented by the following formula in copolymerized relationship with units of at least one other ethylenically unsaturated monomer:



wherein R¹ and R² are hydrogen atoms or lower alkyl groups and R² can additionally be a group containing at least one aromatic nucleus; Q can be a covalent bond, a divalent alkylene radical, a divalent arylene radical, a divalent aralkylene radical, a divalent arylenealkylene radical,



wherein R⁶ is an alkylene radical, or R² can be taken together with Q to form a



group; R³, R⁴ and R⁵ can be lower alkyl or aryl groups, or R³ and R⁴ and the nitrogen atom to which they are attached can be taken together to represent the atoms and bonds necessary to form a quaternized nitrogen-containing heterocyclic ring which is attached to Q, and X[⊖] is a monovalent negative salt-forming radical or atom; wherein said polymer is substantially free of carboxy groups.

19. The process of claim 18 wherein each said basic polymeric mordant is copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride].

20. The process of claim 17 wherein each said basic polymeric mordant comprises copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride].

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

I. imagewise-exposing a photosensitive element comprising a support having thereon:

- 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;
- an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent;
- a direct-positive, green-sensitive silver halide emulsion layer containing a nondiffusible cou-

pler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;

- an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent; and
- 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 nondiffusible coupler having the formula: DYE-LINK-(COUP-BALL)_n or BALL-LINK-(COUP-SOL)_n, wherein:

- DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
- 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;
- 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;
- 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;
- 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
- 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. superposing over said blue-sensitive silver halide emulsion layer after exposure of said photosensitive element a dye image-receiving element comprising a support having thereon a dye image-receiving layer;

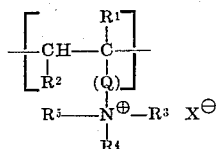
III. positioning a rupturable container containing an alkaline processing composition comprising an aromatic primary amino color developing agent between said exposed photosensitive element and said dye image-receiving layer;

IV. 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;

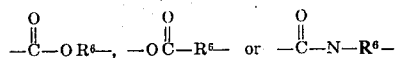
V. forming an imagewise distribution of diffusible dye image-providing material as a function of said imagewise exposure of each said silver halide emulsion layer; and

VI. at least a portion of each said imagewise distribution of diffusible dye image-providing material diffusing to said dye image-receiving layer;
the improvement comprising employing as said dye image-receiving element a support having thereon a polymeric acidic material layer, a light-reflecting layer comprising a basic polymeric mordant and an opacifying agent, and a dye image-receiving layer comprising a basic polymeric mordant.

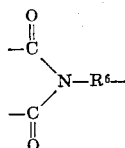
22. The process of claim 21 wherein each said basic polymeric mordant comprises a polymer having at least one-third of the units represented by the following formula in copolymerized relationship with units of at least one other ethylenically unsaturated monomer:



wherein R¹ and R² are hydrogen atoms or lower alkyl groups and R² can additionally be a group containing at least one aromatic nucleus; Q can be a covalent bond, a divalent alkylene radical, a divalent arylene radical, a divalent aralkylene radical, a divalent arylenealkylene radical,



wherein R⁶ is an alkylene radical, or R² can be taken together with Q to form a



group; R³, R⁴ and R⁵ can be lower alkyl or aryl groups, or R³ and R⁴ and the nitrogen atom to which they are attached can be taken together to represent the atoms and bonds necessary to form a quaternized nitrogen-containing heterocyclic ring which is attached to Q; and X[⊖] is a monovalent negative salt-forming radical or atom; wherein said polymer is substantially free of carboxy groups and wherein the positive salt-forming radical of said polymer comprises at least two aryl groups for each quaternary nitrogen atom in said polymer and said opacifying agent comprises titanium dioxide.

23. A reception element comprising a support having thereon:

1. a light-reflecting layer comprising a basic polymeric mordant and an opacifying agent and
2. a dye image-receiving layer comprising a basic polymeric mordant.

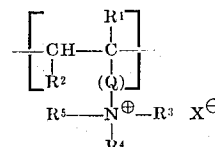
24. The reception element of claim 23 which includes a pH-lowering layer between said support and said layer 1).

25. The reception element of claim 24 wherein said pH-lowering layer comprises a polymeric acid.

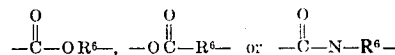
26. The reception element of claim 23 wherein said opacifying agent comprises titanium dioxide.

27. The reception element of claim 25 wherein said opacifying agent comprises titanium dioxide.

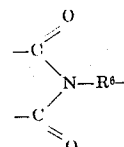
28. The reception element of claim 23 wherein each said basic polymeric mordant comprises a polymer having at least one-third of the units represented by the following formula in copolymerized relationship with units of at least one other ethylenically unsaturated monomer:



wherein R¹ and R² are hydrogen atoms or lower alkyl groups and R² can additionally be a group containing at least one aromatic nucleus; Q can be a covalent bond, a divalent alkylene radical, a divalent arylene radical, a divalent aralkylene radical, a divalent arylenealkylene radical,



wherein R⁶ is an alkylene radical, or R² can be taken together with Q to form a



group; R³, R⁴ and R⁵ can be lower alkyl or aryl groups, or R³ and R⁴ and the nitrogen atom to which they are attached can be taken together to represent the atoms and bonds necessary to form a quaternized nitrogen-containing heterocyclic ring which is attached to Q; and X[⊖] is a monovalent negative salt-forming radical or atom; wherein said polymer is substantially free of carboxy groups.

29. The reception element of claim 28 wherein each said basic polymeric mordant is copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride].

30. The reception element of claim 27 wherein each said basic polymeric mordant is copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride].

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