United States Patent [19]
Wolfarth et al.

[11] **3,725,063**
[45] **Apr. 3, 1973**

[54] DEVELOPER SCAVENGERS FOR IMAGE TRANSFER SYSTEMS

[75] Inventors: **Eugene F. Wolfarth**, Pittsford; **Donald A. Smith**, Rochester; **Charles F. Farran**, Pittsford; **Glen M. Dappen**, Webster, all of N.Y.

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

[22] Filed: **Jan. 13, 1971**

[21] Appl. No.: **106,281**

[52] **U.S. Cl.** ....**96/29 D**, 96/56, 96/77
[51] **Int. Cl.** **G03c 5/54**
[58] **Field of Search**....................96/29, 56

[56] **References Cited**

UNITED STATES PATENTS

3,445,228	5/1969	Beavers et al.	96/29

Primary Examiner—J. Travis Brown
Assistant Examiner—John L. Goodrow
Attorney—Robert W. Hampton, J. R. Frederick and H. E. Cole

[57] ABSTRACT

A developer scavenger layer comprising an isocyanate-bisulfite addition product and a polymeric binder is useful for reducing background stain in a dye image-receiving element of a color diffusion transfer system utilizing immobile couplers which form diffusible dyes.

16 Claims, No Drawings

DEVELOPER SCAVENGERS FOR IMAGE TRANSFER SYSTEMS

This invention relates to the art of photography, and more particularly to color diffusion transfer film systems, dye image-receiving elements and methods for obtaining positive, right-reading diffusion transfer dye images with reduced color developer stain.

U.S. Pat. No. 3,445,228 of Beavers et al., issued May 20, 1969, describes a receiving sheet for use in a dye diffusion transfer process utilizing aromatic primary amino color developing agents. The receiving sheet comprises a support having thereon a nondiffusible acid material, an interlayer containing finely divided white pigment and a mordant layer. The acid layer terminates development by lowering the pH of the alkaline developer composition and apparently also functions to salt out residual color developer. The pigmented layer functions to mask the stain formed in the underlying layer.

It is an object of this invention to provide a novel dye image-receiving element wherein a developer scavenger layer is employed which effectively destroys any residual color developer by forming a colorless reaction product, thereby eliminating the need for a pigmented masking layer.

Another object of this invention is to provide timing means in connection with the developer scavenger layer so that development in the photosensitive element is substantially complete before the developer scavenger layer becomes operative.

It is another object of this invention to reduce the formation of the yellowish-brown stain which appears in color diffusion transfer image-receiving layers and is caused by the aerial oxidation of unused color developer present in the layer.

Still another object of this invention is to provide color transfer film units and methods for processing same wherein the dye image-receiving layer is integral with the photosensitive element itself or is provided on a separate support to be superposed on the photosensitive element after exposure thereof.

These and other objects are achieved by a photographic film unit according to our 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;

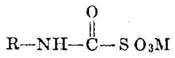
b. a dye image-receiving layer; and

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 the pressure-applying members will effect a discharge of the container's contents within the film unit;

the above film unit containing an aromatic primary amino color developing agent, preferably in the rupturable container, and an isocyanate-bisulfite addition product in a polymeric binder which is capable of reacting with unused aromatic primary amino color developing agent to form a colorless urea reaction product.

The developer-scavenging, isocyanate-bisulfite addition products or adducts employed in our invention have the following general formula:

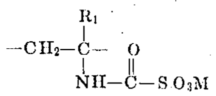
(I)



$$R-NH-\overset{O}{\overset{\|}{C}}-SO_3M$$

or polymers or copolymers having recurring units of the following formula:

(II)



$$-CH_2-\overset{R_1}{\overset{|}{\underset{NH-\overset{O}{\overset{\|}{C}}-SO_3M}{\underset{|}{C}}}}-$$

wherein R represents an acyclic alkyl group, including a substituted acyclic alkyl group, preferably a lower acyclic alkyl group, i.e., having one to six carbon atoms in the chain such as methyl, ethyl, isopropyl, benzyl, hexyl, carbethoxymethyl, etc.; an alkenyl group such as vinyl, isopropenyl, allyl, etc., preferably having one to six carbon atoms; an alicyclic group typically having four to six carbon atoms in the ring such as cyclohexyl, cyclopentyl, cyclobutyl, etc.; or an aryl group, including a substituted aryl group, such as phenyl, tolyl, naphthyl, methoxyphenyl, biphenylyl, etc.;

R_1 represents a hydrogen atom or an alkyl group, including a substituted alkyl group as described above for R; and

M represents an alkali metal ion, e.g., a sodium, potassium or ammonium ion.

In a preferred embodiment, R can be substituted with a second —$NHCOSO_3M$ group to provide bis(isocyanate-bisulfite)-addition products.

Examples of monomeric, developer-scavenging, isocyanate-bisulfite addition products or salt adducts coming within the scope of Formula I include:

$CH_3NHCOSO_3Na$

methyl isocyanate sodium bisulfite adduct

$CH_3CH_2NHCOSO_3Na$

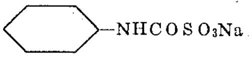
ethyl isocyanate sodium bisulfite adduct

$CH_3CH_2OOCCH_2NHCOSO_3Na$

ethyl isocyanatoacetate sodium bisulfite adduct

$(CH_3)_2CHNHCOSO_3Na$

isopropyl isocyanate sodium bisulfite adduct



cyclohexyl isocyanate sodium bisulfite adduct

$CH_3(CH_2)_5NHCOSO_3Na$

n-hexyl isocyanate sodium bisulfite adduct

$NaSO_3CONH(CH_2)_6NHCOSO_3Na$

hexamethylene diisocyanate bis sodium bisulfite adduct

$(CH_3)_2CHNHCOSO_3K$

isopropyl isocyanate potassium bisulfite adduct

$KSO_3CONH(CH_2)_6NHCOSO_3K$

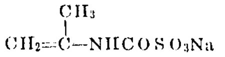
hexamethylene diisocyanate bis potassium bisulfite adduct

$C_6H_5NHCOSO_3Na$

phenyl isocyanate sodium bisulfite adduct

$CH_2{=}CHNHCOSO_3Na$

vinyl isocyanate sodium bisulfite adduct

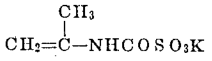


$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}NHCOSO_3Na$

isopropenyl isocyanate sodium bisulfite adduct

$CH_2{=}CHNHCOSO_3K$

vinyl isocyanate potassium bisulfite adduct



$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}NHCOSO_3K$

isopropenyl isocyanate potassium bisulfite adduct

Examples of polymers and copolymers within the scope of formula II above include homopolymers of vinyl isocyanate sodium bisulfite adducts or isopropenyl isocyanate sodium bisulfite adducts and copolymers of these adducts with vinyl compounds such as unsaturated acids, e.g., acrylic acid and methacrylic acid; acrylic esters, e.g., methyl acrylate and propyl acrylate; methacrylic esters, e.g., methyl methacrylate and ethyl methylacrylate; acrylamides, e.g., acrylamide and isopropyl acrylamide; and methacrylamides, e.g., methacrylamide, and N-methyl-methyacrylamide.

The described developer-scavenging, isocyanate-bisulfite adducts can be employed at any concentration useful for the intended purpose. Generally, an effective concentration is from about 300 mg per square foot of support to about 750 mg per square foot of support. Especially good results are obtained at a concentration of from about 400 mg per square foot of support to about 600 mg per square foot of support.

The isocyanate-bisulfite addition product of our invention may be dispersed in any polymeric binder suitable for the intended purpose, e.g., gelatin, proteins, cellulose derivatives, polysaccharides, polyvinyl compounds, acrylamide polymers and copolymers, etc. In addition, in embodiments of our invention where the developer scavenger material itself is a polymer, no additional polymeric binder may be needed, i.e., the polymeric scavenger material can serve as the polymeric binder.

It is believed that the bisulfite adduct functions as a developer scavenger precursor and under the basic conditions of color development reverts to the parent isocyanate compound which in turn reacts with excess unused aromatic primary amino color developing agent to form a colorless product, thereby reducing the yellowish-brown stain which results from the diffusion of unused aromatic primary amino color developing agent into the image-receiving element. Therefore, any isocyanate bisulfite addition product which is compatible with the photosensitive and image-receiving elements can be employed in the practice of the invention provided the addition product reverts under alkaline conditions to the parent isocyanate compound which in turn will react with primary amino color developing agent to form a colorless product.

The developer scavenger layer of our 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 our invention wherein the image-receiving element is separate from the photosensitive element, the novel dye image-receiving element comprises a support having thereon the following layers:

a. a developer-scavenger layer comprising an isocyanate-bisulfite adduct in a polymeric binder, and

b. a dye image-receiving layer.

A timing layer, described hereinafter, can also be employed in the invention between the developer-scavenging layer and the dye image-receiving layer which functions to delay the rate of diffusion of aromatic primary amino color developing agent into the developer-scavenging layer. The timing layer, therefore, ensures the efficient use of the aromatic primary amino color developing agent in the photosensitive element prior to developer-scavenging action by the isocyanate-bisulfite adduct. A pH-lowering material, described hereinafter, can also be employed in the dye image-receiving element to increase the stability of the transferred image.

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 element. 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 our invention, the image dyes 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. The timing layer, if one is present, prevents the diffusion of color developer into the scavenger layer for the time necessary to ensure the efficient use of the aromatic primary amino color developing agent in the photosensitive element. Upon separation, it is believed that the unused aromatic primary amino color developing agent diffuses into the developer-scavenger layer where the developer molecules react with the isocyanate compounds which have been liberated from the isocyanate-bisulfite adducts under alkaline conditions of development to form a colorless product. Regardless of the mechanism involved, a marked decrease in the yellowish-brown stain caused by the presence of unused color developing agent in color development diffusion transfer image-receiving elements is observed upon utilizing a developer-scavenger layer comprising an isocyanate bisulfite adduct dispersed in a suitable binder, preferably in the image-receiving element.

In another embodiment of our invention, the developer-scavenger layer can be located in an integral film unit wherein 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. 27,991 of Barr, Bush and Thomas, filed Apr. 13, 1970. 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, a developer scavenger layer comprising an isocyanate-bisulfite adduct dispersed in a suitable binder, 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 superposed 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. It is believed that positioning of the developer-scavenger layer between the color-forming photosensitive units and the image-receiving layer in the integral receiver-negative film system prevents the diffusion of unused color developer into the image-receiving layer. If desired, an auxiliary developer scavenger layer comprising the isocyanate-bisulfite adducts described herein can be located on the opaque process sheet. 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. 27,991 of Barr, Bush and Thomas, filed Apr. 13, 1970.

Another embodiment of integral receiver-negative photosensitive systems in which our invention can be employed is described in U.S. Ser. No. 27,990 of Cole, filed Apr. 13, 1970. 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, a developer scavenger layer comprising an isocyanate-bisulfite adduct dispersed in a suitable binder, 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 a 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. Any unused aromatic primary amino color developing agent, which may diffuse in the direction of the image-receiving layer, is immobilized by the isocyanate-bisulfite adduct present in the developer scavenger layer. Any undesirable products formed in the developer-scavenger layer are masked from the viewer by the opaque light-reflective layer. 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. 27,990.

In the photographic film units according to our 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 alkaline processing composition.

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

$$\text{DYE} - \text{LINK} - (\text{COUP} - \text{BALL})_n$$

and,

$$\text{BALL} - \text{LINK} - (\text{COUP} - \text{SOL})_n$$

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

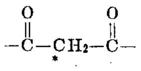
6. *n* is an integer of 1 to 2 when LINK is an alkylidene radical, and *n* is 1 when LINK is an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical or an azoxy radical.

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 eight 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, coupler 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.,



$$-\overset{O}{\overset{\|}{C}}-\underset{*}{C}H_2-\overset{O}{\overset{\|}{C}}-$$

*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.

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 attached 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 receiver portion of the film unit. 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 emulsions 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. 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 transparent 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).

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 one liter.	

DEVELOPER B

P-hydroxyphenylglycine	10 g.
Sodium carbonate	100 g.
Water to make one 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, 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, 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, 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, Feb. 13, 1951, shows 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 μ wavelength preferably 520–554 μ, to substantially destroy 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 and French Pat. No. 1,520,821.

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. No. 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 application Ser. No. 828,064 filed Apr. 28, 1969; 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 grams per liter of developer if it is located in the developer. Other embodiments of our invention employ the photosensitive elements described in the above-mentioned U.S. Pat. Nos. 3,227,550; 3,227,551; 3,227,552; and in British Pat. No. 904,364 P.19 lines 1–41. These embodiments all employ the nondiffusible couplers described above.

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. 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; and Taber et al. U.S. Pat. No. 3,384,486. 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 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, 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 and Jones et al. U.S. Pat. No. 2,937,089.

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, 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; Illingsworth U.S. Pat. No. 3,320,069; and McBride U.S. Pat. No. 3,271,157. Emulsions that contain silver halide grains having substantial surface sensitivity can be used, and emulsions that contain silver halide grains having substantial sensitivity inside the grains can be used such as those described in Davey et al. U.S. Pat. No. 2,592,250; Porter et al. U.S. Pat. No. 3,206,313; and Bacon et al. U.S. Pat. No. 3,447,927. The emulsions can be regular grain emulsions such as the type described in Klein and Moisar, *J. Phot.Sci.*, Volume 12, No. 5, Sept./Oct., 1964, pp. 242–251. Negative-type emulsions can be used or direct positive emulsions can be used such as those described in Leermakers U.S. Pat. No. 2,184,013; Kendall et al. U.S. Pat. No. 2,541,472; Berriman U.S. Pat. No. 3,367,778; Schouwenaars British Pat. No. 723,019; Illingsworth et al. French Pat. No. 1,520,821; Ives U.S. Pat. No. 2,563,785; Knott et al. U.S. Pat. No. 2,456,953 and Land U.S. Pat. No. 2,861,885.

The emulsions used in this invention can 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; Waller et al. U.S. Pat. No. 2,399,083; McVeigh U.S. Pat. No. 3,297;447; and Dunn U.S. Pat. No. 3,297,446.

The silver halide emulsions used in 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; Dann et al. U.S. Pat. No. 3,046,134; Carroll et al. U.S. Pat. No. 2,944,900; and Goffe U.S. Pat. NO. 3,294,540.

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 and Allen et al. U.S. Pat. No. 2,694,716; the azaindenes described in Piper U.S. Pat. NO. 2,886,437 and Heimbach et al. U.S. Pat. No. 2,444,605; the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,663; the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652; the oximes described in Carroll et al. British Pat. No. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927; Kennard et al. U.S. Pat. No. 3,266,897 and Luckey et al. U.S. Pat. No. 3,397,987; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405; the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839; and the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263 and Yutzy et al. U.S. Pat. No. 2,597,915.

In the above-described embodiments employing non-diffusible 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 4-amino-N,N-diethyl-3-methyl aniline hydrochloride, N,N-diethyl-p-phenylenediamine, 2-amino-5-diethylamino toluene, N-ethyl-β-methane-sulfonamidoethyl-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-hydroxyethyl)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 sulfate salt, 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; 2,643,886; 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 processing solution 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; 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 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 methacrylate, those which have cross-linking sites which facilitate hardening or curing, and those which have recurring sulfobetaine units as described in Dykstra Canadian Pat. No. 774,054.

Any material can be employed as the image-receiving layer in this invention as long as the desired function of mordanting or otherwise fixing the dye images will be obtained. 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 the Minsk U.S. Pat. No. 2,882,156 granted Apr. 14, 1959. Other mordants useful in our invention include poly-4-vinylpyridine, the 2-vinyl pyridine polymer metho-p-toluene sulfonate and similar compounds described in Sprague et al. U.S. Pat. No. 2,484,430 granted Oct. 11, 1949, and cetyl trimethylammonium bromide, etc. Effective mordanting compositions are also described in Whitmore U.S. Pat. No. 3,271,148 and Bush U.S. Pat. No. 3,271,147.

Furthermore, the image-receiving layer can be sufficient by itself to mordant the dye as in the case of use of an alkaline solution-permeable polymeric layer such as N-methoxymethyl polyhexylmethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate; gelatin; and other materials of a similar nature. Generally, good results are obtained when the image-receiving layer, preferably alkaline solution-permeable, is transparent and about 0.25 to about 0.04 mil in thickness. This thickness, of course, can be modified depending upon the result desired. The image-receiving layer can also contain ultraviolet absorbing materials to protect the mordanted dye images from fading due to ultraviolet light and/or brightening agents such as the stilbenes, coumarins, triazines, oxazoles, etc.

Use of a pH-lowering material in 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 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 or metallic salts, e.g., zinc acetate or solid acids 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 development to terminate further dye transfer and thus stabilize the dye image. The pH-lowering material can be present as a separate layer between the scavenger layer and the support or it can be contained in the scavenger layer if desired.

An inert timing or spacer layer can be employed in our invention between the developer scavenger layer and the dye image-receiving layer which "times" or controls the scavenging reaction as a function 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 effective in evening out the various reaction rates over a wide range of temperatures, e.g., premature pH reduction is prevented when imbibition is effected at temperatures 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. Especially good results are obtained when the timing layer comprises a hydrolyzable polymer or a mixture of such polymers which are slowly hydrolyzed by the processing composition. Examples of such hydrolyzable polymers include polyvinyl acetate, polyamides, polyvinyl ethers, partial acetate of polyvinyl alcohol, 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. 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. In certain embodiments of our invention, an opacifying agent, e.g., TiO_2, carbon black, etc. may be added to the processing composition.

While the alkaline processing composition used in this invention can be employed in a rupturable container, as described previously, to conveniently facilitate the introduction of processing composition into the film unit, other methods of inserting processing composition into the film unit could also be employed, e.g., interjecting processing solution with communicating members similar to hypodermic syringes which are attached either to a camera or camera cartridge.

The alkaline solution-permeable, substantially opaque, light-reflective layer employed in certain embodiments of integral photographic film units of our invention can generally comprise any opacifier dispersed in a binder as long as it has the desired properties. Particularly desirable are white light-reflective layers since they would be esthetically pleasing backgrounds on which to view a transferred dye image and would also 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. The opacifying agents may be dispersed in any binder such as an alkaline solution-permeable polymeric matrix such as, for example, gelatin, polyvinyl alcohol, and the like. Brightening agents such as the stilbenes, coumarins, triazines and oxazoles can also be added to the light-reflective layer, if desired. When it is desired to increase the opacifying capacity of the light-reflective layer, dark-colored opacifying agents may be added to it, e.g., carbon black, nigrosine dyes, etc.

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(ethyleneterephthalate) film, polycarbonate film, poly-α-olefins such as polyethylene and polypropylene film, and related films or resinous materials as well as glass. 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 can contain surfactants such as saponin, anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. No. 2,600,831; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 3,133,816; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson 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; Gaspar U.S. Pat. No. 2,274,782; Silverstein et al. U.S. Pat. No. 2,527,583 and VanCampen U.S. Pat. No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton et al. U.S. Pat. No. 3,282,699.

The sensitizing dyes and other addenda used in the practice of this invention can be added from water solutions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including those described in Collins et al. U.S. Pat. No. 2,912,343; McCrossen et al. U.S. Pat. No. 3,342,605; Audran U.S. Pat. No. 2,996,287 and Johnson et al. U.S. Pat. No. 3,425,835.

The photographic layers used in the practice of this invention can 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. If desired, two or more layers can be coated simultaneously by the procedures described in Russell U.S. Pat. No. 2,761,791 and Wynn British Pat. No. 837,095. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat No. 968,453 and Lu Valle et al. U.S. Pat. No. 3,219,451.

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, ketones, carbocyclic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefin, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

The following examples further illustrate the invention.

EXAMPLE 1

A multilayer, multicolor photosensitive element is prepared by coating the following layers in the order recited on an opaque cellulose acetate film support:

1. Red-sensitive internal image gelatin-silver chlorobromide emulsion (171 mg. gelatin/ft^2 and 110 mg. silver/ft^2), cyan image transfer coupler 1-hydroxy-4-{4-[α-(3-pentadecylphenoxy(butyramido]phenoxy}-N-ethyl-3',5'-dicarboxy-2-naphthanilide (120 mg/ft^2) and a fogging agent formyl-4-methylphenylhydrazine (0.5 g/mole of silver chlorobromide)

2. A scavenger interlayer comprising 1-hydroxy-N-[α-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide (45 mg/ft^2), tri-cresyl phosphate (23 mg/ft^2) and gelatin (65 mg/ft^2)

3. Green-sensitive internal image silver chlorobromide emulsion (116 mg. gelatin/ft^2 and 100 mg. silver/ft^2), magenta image transfer coupler 1-phenyl-3-[(3,5-dicarboxyanilino)octadecylcarbamylphenylthio]-5-pyrazolone (80 mg/ft^2), N-n-butylacetanilide (40 mg/ft^2) and a fogging agent formyl-4-methylphenylhydrazine (0.5 g/mole of silver chlorobromide)

4. A scavenger and a yellow filter layer comprising 1-hydroxy-N-[α-(2,4-di-tert-amylphenoxy)butyl]-2 naphthamide (50 mg/ft^2), tri-cresyl phosphate (25 mg/ft^2), yellow Carey Lea silver (15 mg/ft^2) and gelatin (65 mg/ft^2)

5. Blue-sensitive internal image gelatin-silver chlorobromoiodide emulsion (126 mg gelatin/ft^2 and 100 mg silver/ft^2), yellow image transfer coupler α-pivalyl-α-(4-nitro-3-pentadecyl-phenoxy)-4-sulfamylacetanilide (100 mg/ft^2), N-n-butylacetanilide (50 mg/ft^2) and fogging agent formyl-4-methylphenylhydrazine (0.5 g/mole of silver chlorobromide).

6. Overcoat of gelatin (50 mg/ft^2) and 1-hydroxy-N-[α-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide (20 mg/ft^2).

A multilayer dye image-receiving element is prepared by coating the following layers in the order recited on an opaque cellulose acetate film support:

1. a pH-lowering layer of copoly(methyl acrylate, gamma-sulfo propylacrylate sodium salt, 2-acetoacetoxyethyl methacrylate) (500 mg/ft^2) and zinc acetate (300 mg/ft^2),

2. developer scavenger layer of hexamethylene diisocyanate bis sodium bisulfite adduct (500 mg/ft^2) and copoly(methyl acrylate, gamma-sulfopropylacrylate sodium salt, 2-acetoacetoxyethyl methacrylate) (500 mg/ft^2),

3. a timing layer of cellulose acetate and cellulose acetate hexahydrophthalate (200 mg/ft^2),

4. a gelatin interlayer (25 mg/ft^2) and

5. an image-receiving layer of copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimiodopropyl)ammonium chloride] (200 mg/ft^2) and poly(vinyl alcohol) (200 mg/ft^2).

A control dye image-receiving element is prepared but without developer scavenger layer 2.

Two samples of the photosensitive element are exposed to a graduated-density multicolor test object. The following processing composition is employed in a pod and is spread between the exposed surface of the photosensitive element and each superposed dye image-receiving element by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers:

potassium hydroxide	35 g.
4-Amino-N-ethyl-N-β-hydroxyethyl-aniline sulfate	40 g.
piperidino hexose reductone	0.20 g.
5-methylbenzotriazole	0.05 g.
Hydroxyethylcellulose	30 g.
distilled water to	1000 ml.

After 60 seconds at about 20°C. the film units are separated. The dye image-receiving elements are then kept for 24 hours at 60°C/70% R.H. The background densities of the two elements are then measured. The background density of the dye image-receiving element of the invention is 83 percent less than the background density observed with the control dye image-receiving element which does not contain the developer scavenger layer.

EXAMPLE 2

This example illustrates the use of a polymeric isocyanatebisulfite adduct as a developer-scavenger precursor.

A multilayer, multicolor photosensitive element is prepared according to the procedure described in Example 1 except that a blue sensitive gelatin-silver chlorobromide emulsion (126 mg gelatin/ft^2 and 100 mg silver/ft^2) is substituted for the silver chlorobromoiodide emulsion in layer 5 of Example 1.

A multilayer dye image-receiving element is prepared by coating the following layers in the order recited on an opaque cellulose acetate film support:

1. a pH-lowering layer of copoly(butylacrylate, sodium 2-methacryloxyethyl sulfate, 2-acetoacetoxyethyl methacrylate, 500 mg/ft^2) and zinc acetate (500 mg/ft^2),

2. developer-scavenger layer of copoly(vinyl isocyanate sodium bisulfite adduct-isopropylacrylamide) (65 percent vinyl isocyanate adduct content), (500 mg/ft^2) and copoly-(butylacrylate, sodium 2-methacryloxyethyl sulfate, 2-acetoacetoxyethyl methacrylate, (500 mg/ft^2),

3. a timing layer similar to layer 3 of Example 1,

4. a gelatin interlayer (25 mg/ft^2), and

5. an image-receiving layer similar to layer 5 of Example 1.

A control dye image-receiving element is prepared but without developer scavenger layer 2.

Two samples of the photosensitive element are exposed and processed as in Example 1. The elements are oven-tested as in Example 1 and then the background densities measured. The background density of the dye image-receiving element of the invention is 60 percent less than the background density observed with the control dye image-receiving element which does not contain the developer scavenger layer.

EXAMPLE 3

This example demonstrates that the structure of the dye image-receiving element can be simplified without lessening the ability of the isocyanate-bisulfite adduct to function as a developer scavenger.

The procedure as described in Example 2 is followed with the exception that layers 1 and 2 of the dye image-receiving layer are combined into a single layer. In this case, the background density of the dye image-receiving elements of the invention after 24 hrs. at 60°C./70% R.H. is 64 percent less than the background density observed with a dye image-receiving element of the same configuration, but without the isocyanate-bisulfite adduct scavenger layer.

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

We 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:

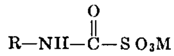
a. a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer, each said silver halide emulsion layer having associated therewith a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible dye;

b. a dye image-receiving layer; 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 developing agent scavenger layer comprising an isocyanate-bisulfite addition product in a polymeric binder, said isocyanate-bisulfite addition product having the formula:

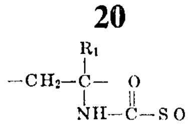
(I)



$$R-NH-\overset{O}{\overset{\|}{C}}-SO_3M$$

or polymers and copolymers having recurring units of the following formula:

(II)



$$-CH_2-\overset{R_1}{\overset{|}{\underset{NH-\overset{O}{\overset{\|}{C}}-SO_3M}{\underset{|}{C}}}}-$$

wherein R represents an acyclic alkyl group, an alkenyl group, an alicyclic group, or an aryl group;

R_1 represents a hydrogen atom or an alkyl group; and M represents an alkali metal ion.

2. The 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 film unit of claim 2 wherein said dye image-receiving layer is located in said photosensitive element between said support and the lowermost photosensitive silver halide emulsion layer, and said scavenger layer is located in said photosensitive element between said dye image-receiving layer and said lowermost photosensitive silver halide emulsion layer.

4. The film unit of claim 2 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, and said scavenger layer is located between said dye image-receiving layer and its said support.

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 4 which contains a timing layer between said scavenger layer and said dye image-receiving layer.

7. The film unit of claim 4 which also contains a pH-lowering material.

8. The film unit of claim 1 wherein R is substituted with a second —NHCOSO$_3$M group.

9. The film unit of claim 8 wherein said isocyanate-bisulfite addition product is hexamethylene diisocyanate bis sodium bisulfite adduct.

10. The film unit of claim 1 wherein said isocyanate bisulfite addition product is copoly(vinyl isocyanate-sodium bisulfite adduct—isopropylacrylamide).

11. 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

DYE — LINK — (COUP — BALL)$_n$

or

BALL — LINK — (COUP — SOL)$_n$

wherein:

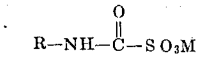
1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an ozoxy 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 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 unit containing an aromatic primary amino color developing agent; the improvement comprising employing between said dye image-receiving layer and its said support a developing agent scavenger layer comprising an isocyanate-bisulfite addition product in a polymeric binder, said isocyanate-bisulfite addition product having the formula:

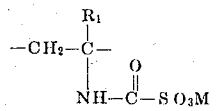
(A)



$$R-NH-\overset{O}{\overset{\|}{C}}-SO_3M$$

or polymers and copolymers having recurring units of the following formula:

(B)



$$-CH_2-\overset{R_1}{\underset{NH-\overset{O}{\overset{\|}{C}}-SO_3M}{C}}-$$

wherein R represents an acyclic alkyl group, an alkenyl group, an alicyclic group, or an aryl group; R$_1$ represents a hydrogen atom or an alkyl group; and M represents an alkali metal ion.

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;

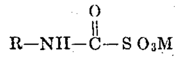
B. treating the layer outermost from the support of said photosensitive element with an alkaline processing composition to effect development of each of said exposed silver halide emulsion layers with an aromatic primary amino color developing agent,

C. 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

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

the improvement comprising employing a developing agent scavenger layer comprising an isocyanate-bisulfite addition product in a polymeric binder, said isocyanate-bisulfite addition product having the formula:

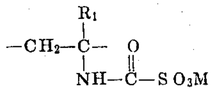
(I)



$$R-NH-\overset{O}{\overset{\|}{C}}-SO_3M$$

or polymers and copolymers having recurring units of the following formula:

(II)



$$-CH_2-\overset{R_1}{\underset{NH-\overset{O}{\overset{\|}{C}}-SO_3M}{C}}-$$

wherein R represents an acyclic alkyl group, an alkenyl group, an alicyclic group, or an aryl group;

R_1 represents a hydrogen atom or an alkyl group; and

M represents an alkali metal ion.

13. The process of claim **12** 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; said scavenger layer being located between said dye image-receiving layer and its said 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.

14. The process of claim **13** wherein R is substituted with a second $—NHCOSO_3M$ group.

15. The process of claim **14** wherein said isocyanate-bisulfite addition product is hexamethylene diisocyanate bis sodium bisulfite adduct.

16. The process of claim **13** wherein said isocyanate-bisulfite addition product is copoly(vinyl isocyanate sodium bisulfite adduct—isopropylacrylamide).

* * * * *