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Janssen et al.

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[54] **DEVELOPMENT ACCELERATORS FOR IMAGE TRANSFER SYSTEMS**

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[52] **U.S. Cl.**.....**96/29 D,** 96/3, 96/66.3

[51] **Int. Cl.**.....**G03c 1/48,** G03c 5/54, G03c 7/00

[58] **Field of Search**.....96/29 D, 3, 76 C, 66 R, 66.3

[56] **References Cited**

UNITED STATES PATENTS

3,462,266 8/1969 Stewart.....96/29 D

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Assistant Examiner—Alfonso T. Suro Pico
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[57] **ABSTRACT**

A development accelerator comprising a 2-substituted aminomethyl-5-alkylhydroquinone or salt thereof increases the maximum density in a direct-positive color diffusion transfer system utilizing immobile couplers which form diffusible dyes.

27 Claims, No Drawings

DEVELOPMENT ACCELERATORS FOR IMAGE TRANSFER SYSTEMS

This invention relates to the art of photography, and more particularly to color diffusion transfer film systems, photosensitive elements and methods for obtaining positive, right-reading diffusion transfer dye images with increased maximum dye densities.

U.S. Pat. No. 3,227,552 of Whitmore issued Jan. 4, 1966, describes a color diffusion transfer system utilizing direct-positive, silver halide emulsions and nondiffusible couplers which react with an oxidized color developing agent to form diffusible dyes. In columns 4 and 5 of that patent, there are described certain sulfonated hydroquinones which are employed to increase the maximum dye densities. It would be desirable to find other compounds which would increase maximum dye densities and which would also be superior to the sulfonated hydroquinones described therein.

U.S. Pat. No. 3,243,294 of Barr issued Mar. 29, 1966, describes certain diffusible hydroquinones having at least one amino-substituted lower alkyl group utilized as a black-and-white developing agent in a color diffusion transfer system. The silver halide emulsions employed therein are described as conventional developing-out, negative-type emulsions and contain physical development nuclei. The hydroquinone develops the latent image to form a negative silver image. The undeveloped silver halide is thereafter physically developed by a color developing agent to form a positive color image. The hydroquinones are not employed in this patent as development accelerators, however, and are not employed with direct-positive silver halide emulsions.

U.S. Pat. No. 3,411,904 of Becker issued Nov. 19, 1968, and No. 3,462,266 of Stewart issued Aug. 19, 1969, describe various hydroquinones utilized in dye developer diffusion transfer systems. Those hydroquinones and imaging chemistry are distinguishable, however, from the color system described by the instant invention.

It is an object of this invention to provide a development accelerator for a color diffusion transfer system utilizing direct-positive, silver halide emulsions and nondiffusible couplers which produce diffusible dyes.

It is another object of this invention to provide photosensitive elements, film units and methods for obtaining a transfer image wherein a development accelerator is utilized in the photosensitive element.

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 direct-positive, silver halide emulsion layers, each silver halide emulsion layer having associated therewith a dye image-providing material

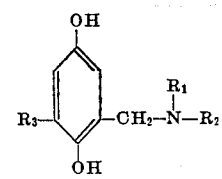
comprising a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible dye, the photosensitive element containing a 2-substituted aminomethyl-5-alkylhydroquinone or salt thereof;

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.

The 2-substituted aminomethyl-5-alkylhydroquinones utilized in our invention may be represented by the following formula:



wherein R_3 is an alkyl group, including substituted alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, octyl, hexyl, nonyl, decyl, dodecyl, octadecyl, aralkyl such as benzyl, methylbenzyl, phenethyl, etc. Preferably R_3 is an alkyl group of at least 8 carbon atoms. R_1 and R_2 are each hydrogen; alkyl, including substituted alkyl groups such as methyl, propyl, isopropyl, butyl, isobutyl, hexyl, 2-ethylhexyl, nonyl, decyl, dodecyl, etc.; hydroxyalkyl; aminoalkyl; aralkyl such as benzyl, methylbenzyl, phenethyl, etc.; cycloalkyl such as cyclopentyl, cyclohexyl, methylcyclohexyl, etc.; alkenyl such as allyl, 2-butenyl, 3-butenyl, etc.; aryl, including substituted aryl such as phenyl, naphthyl, alkaryl such as para-tolyl, etc.; or may be taken together with the nitrogen to which they are attached to represent a heterocyclic ring, especially a 5- or 6-member saturated heterocyclic nucleus such as morpholino, pyrrolidino, piperidino, piperazino, N-methyl piperazino, etc. Preferably, R_1 is hydrogen or methyl and R_2 contains from two to 18 carbon atoms.

Compounds within the above definition include the following:

I. 2-(n-octylaminomethyl)-5-methylhydroquinone
II. 2-(octadecylaminomethyl)-5-methylhydroquinone
III. 2-(n-octylaminomethyl)-5-tert-butylhydroquinone
IV. 2-(n-octylaminomethyl)-5-tert-octylhydroquinone
V. 2-octadecylaminomethyl-5-tert-octylhydroquinone
VI. 2-octadecylaminomethyl-5-tert-butylhydroquinone
VII. 2-ethylaminomethyl-5-octadecylhydroquinone
VIII. 2-isobutylaminomethyl-5-octadecylhydroquinone
IX. 2-allylaminomethyl-5-octadecylhydroquinone
X. 2-(N-allyl-N-methylaminomethyl)-5-octadecylhydroquinone
XI. 2-(N-allyl-N-methylaminomethyl)-5-octadecylhydroquinone
XII. 2-isopropylaminomethyl-5-octadecylhydroquinone
XIII. 2-morpholinomethyl-5-tert-octylhydroquinone
XIV. 2-morpholinomethyl-5-octadecylhydroquinone
XV. 2-piperidinomethyl-5-tert-octylhydroquinone

XVI. 2-piperidinomethyl-5-octadecylhydroquinone
XVII. 2-pyrrolidinomethyl-5-tert-octylhydroquinone
XVIII. 2-pyrrolidinomethyl-5-octadecylhydroquinone
XIX. 2-(4-methylpiperazinomethyl)-5-tert-octylhydroquinone
XX. 2-(4-methylpiperazinomethyl-5-octadecylhydroquinone

Of the above compounds, especially good results are obtained with compounds X, XI AND XIV.

Many of the above compounds, their preparation and use in other diffusion transfer systems are described and claimed in copending U.S. applications Ser. Nos. 863,362 of Reynolds filed Oct. 2, 1969, now abandoned, and 37,907 of Reynolds and Cossar filed May 15, 1970.

As noted above, salts of the above compounds can also be utilized in our invention. Such salts, e.g., HCl, HBr, H_2SO_4, fluoroborate, etc., are more stable, less subject to oxidation, and present a convenient way to incorporate these compounds in a photosensitive element. They may be present in the silver halide emulsion itself or in a layer contiguous thereto. They may be present in any one or all three silver halide emulsion layers in a multicolor element. Our development accelerators may be present in any concentration effective for the intended purpose. Generally, about 0.1 to about 10.0 mg., preferably about 0.5 to about 5mg., of the development accelerator per square foot of silver halide emulsion layer will provide good results.

The development accelerator employed in 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.

The general configuration of an image-receiving layer located on a separate support adapted to be superposed on the photosensitive element after exposure thereof is disclosed, for example, in U.S. Pat. No. 3,362,819. In such an embodiment, a rupturable container is usually positioned during processing of the film unit so that a compressive force applied to the container by pressure-applying members will effect a discharge of the container's contents between the image-receiving element and the outermost layer of the photosensitive element. 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.

In another embodiment of our invention, the dye image-receiving layer is located integral with the photosensitive element between the support and the lowermost photosensitive silver halide emulsion layer. Such integral receiver-negative photosensitive elements are described in copending U.S. application Ser. No. 115,459 of Barr, Bush and Thomas filed Feb. 16, 1971 now abandoned. In such an embodiment, the support for the photosensitive element is transparent and is coated with the dye image-receiving layer, a substantially opaque, light-reflective layer, e.g., TiO_2, and the various layers forming the color-forming units containing a development accelerator as described above. 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. For further details concerning this particular integral film unit, its preparation and use, reference is made to the above-mentioned U.S. application Ser. No. 115,459 of Barr, Bush and Thomas filed Feb. 16, 1971.

Another embodiment of integral receiver-negative photosensitive systems in which our invention can be employed is described in U.S. Ser. No. 115,552 of Cole filed Feb. 16, 1971, now abandoned. In such an embodiment, the support for the color diffusion transfer system is transparent and is coated with the image-receiving layer, a substantially opaque, light-reflective layer, e.g., TiO_2, and then the various layers forming the color-forming units containing a development accelerator as described above 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. For further details concerning this particular integral film unit, its preparation and use, reference is made to the above-mentioned Cole U.S. application Ser. No. 115,552 filed Feb. 16, 1971.

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

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

$$\text{DYE—LINK—(COUP—BALL)}_n \quad \text{and}$$
$$\text{BALL—LINK—(COUP—SOL)}_n$$

wherein:

1. DYE is a dye precursor, e.g., a leuco dye, a "shifted" dye which shifts hypsochromically or bathochromically when subjected to a different en-

vironment such as a change in pH, reaction with a material to form a complex, etc.; or 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

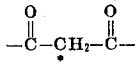
6. *n* is an integer of 1 to 2 when LINK is an alkylidene radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical or an azoxy radical.

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, couple at the carbon atom in the 4-position and the open-chain ketomethylene coupler radicals couple at 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. 106,892 of Bailey et al. filed Jan. 15, 1971.

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 or BALL—S—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— or —S— 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 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, to obtain a positive image on the dye image-receiving layer. 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 emulsions 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. Specific examples of such nondiffusing couplers and other details concerning this type of photographic chemistry are found in U.S. Pat. No. 3,227,550 and No. 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). 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 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, New York, 1942, pages 261–297. Typical methods for the preparation of solarizing emulsions are shown by Groves British Patent 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 Patent 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 mμ wavelength preferably 520–554 mμ, 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; 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 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, application Ser. No. 828,064 filed Apr. 28, 1969 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 grams per liter of developer if it is located in the developer.

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 at al. British Patent 1,154,781 issued June 11, 1969. For optimum results, the dye can either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al, U.S. Pat. No. 2,526,632, issued Oct. 24, 1950; Sprague, U.S. Pat. No. 2,503,776, issued Apr. 11, 1950; Brooker et al., U.S. Pat. No. 2,493,748, issued Jan. 10, 1950; and Taber et al., U.S. Pat. No. 3,384,486 issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri- or tetranuclear) merocyanines, complex (tri- or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g. enamine hemicyanines), oxonols and hemioxonols. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain. The merocyanine dyes can contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoins, rhodanines, 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, and Illingsworth, U.S. Pat. No. 3,320,069 issued May 16, 1967.

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; and 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 Patent 623,448 issued May 18, 1949; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al., U.S. Pat. No. 2,403,927 issued July 16, 1946; Kennard et al., U.S. Pat. No. 3,266,897 issued Aug. 16, 1966; and Luckey et al., U.S. Pat. No. 3,397,987 issued Aug. 20, 1968; the polyvalent metal salts described in Jones, U.S. Pat. No. 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al., U.S. Pat. No. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al., U.S. Pat. No. 2,566,263 issued Aug. 28, 1951; and Yutzy et al., U.S. Pat. No. 2,597,915 issued May 27, 1952; and the tetrazoles described in Hoppe, U.S. Pat. No. 3,352,672, issued Nov. 14, 1967.

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 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-meth-oxy-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, 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 this 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 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 French Patent 2,028,236 or 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 0.5 to 7 microns in thickness or may be contained in the silver halide emulsion layer; and the alkaline solution-permeable polymeric interlayers, e.g., gelatin, are about 0.5 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 those 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 Patent 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 Minsk U.S. Pat. No. 2,882,156 issued Apr. 14, 1959, and basic polymeric mordants such as described in copending U.S. application Ser. No. 100,491 of Cohen et al. filed Dec. 21, 1970. Other mordants useful in 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 issued Oct. 11, 1949, and cetyl trimethyl-ammonium 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, both issued Sept. 6, 1966.

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-methoxy-methyl 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 0.40 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, brightening agents such as the stilbenes, coumarins, triazines, oxazoles, dye stabilizers such as the chromanols, alkylphenols, etc.

Use of a pH-lowering material in the dye image-receiving element of a film unit according to 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 solid acids or metallic salts, e.g., zinc acetate, zinc sulfate, magnesium acetate, etc., as disclosed in U.S. Pat. No. 2,584,030 may be employed with good results. Such pH-lowering materials reduce the pH of the film unit after development to terminate development and substantially reduce further dye transfer and thus stabilize the dye image.

An inert timing or spacer layer can be employed in our invention between the pH-lowering layer and the dye image-receiving layer which "times" or controls the pH-reduction 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 90° 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, cellulose esters, etc.

The alkaline processing composition employed in this invention is the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 12, and preferably containing a developing agent as described previously. The solution also preferably contains a viscosity-increasing compound such as a high-molecular-weight polymer, e.g., a water-soluble ether inert to alkaline solutions such as hydroxyethyl cellulose or alkali metal salts of carboxy-methyl 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 supports for the photographic elements of this invention can be any material as long as it does not deleteriously effect the photographic properties of the film unit and is dimensionally stable. Typical flexible sheet materials include cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethylene-terephthalate) film, polycarbonate film, poly-α-olefins such as polyethylene and polypropylene film, and related films or resinous materials as well as glass, paper, metal, etc. The support is usually about 2 to 6 mils in thickness.

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

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

The various layers, including the photographic layers, employed in the practice of this invention can contain light absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. No. 3,253,921 issued May 31, 1966; Gaspar U.S. Pat. No. 2,274,782 issued Mar. 3, 1942; Silberstein et al. U.S. Pat. No. 2,527,583 issued Oct. 31, 1950; and VanCampen U.S. Pat. No. 2,956,879 issued Oct. 18, 1960.

The sensitizing dyes and other addenda used in the practice of this invention can be added from water solutions or suitable organic solvent solutions may be used. The compounds can be added during various procedures including those described in Collins et al. U.S. Pat. No. 2,912,343 issued Nov. 10, 1959; McCrossen et al. U.S. Pat. No. 3,342,605 issued Sept. 19, 1967; Audran U.S. Pat. No. 2,996,287 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. No. 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, 1965;

Hughes U.S. Pat. No. 3,508,947 issued Apr. 28, 1970; and Wynn British Patent 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. 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 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}) and cyan image transfer coupler 1-hydroxy-4-{4-[α-(3-pentadecylphenoxy)butyr-amido]phenoxy}-N-ethyl-3′,5′-dicarboxy-2-naph-thanilide (120 mg./ft.^{2});
2. a scavenger interlayer comprising 1-hydroxy-N-[α-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide (23 mg./ft.^{2}) and gelatin (65 mg./ft.^{2});
3. green-sensitive internal-image gelatin-silver chlorobromide emulsion (116 mg. gelatin/ft.^{2} and 100 mg. silver/ft.^{2}) and magenta image transfer coupler 1-phenyl-3-octadecylamino-4-[2-phenyl-5-(1,3,4)-oxadiazolylthio]-5-pyrazolone (78 mg./ft.^{2});
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}), yellow Carey Lea silver (15 mg./ft.^{2}) and gelatin (65 mg./ft.^{2});
5. blue-sensitive internal-image gelatin-silver chlorobromoiodide emulsion (171 mg. gelatin/ft.^{2} and 100 mg. silver/ft.^{2}) and yellow image transfer coupler 60-pivaloyl-α-(4-nitro-3-pentadecylphenoxy)-4-sulfoamoylacetanilide (100 mg./ft.^{2}); and
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}).

The above silver halide emulsions are direct-positive emulsions having high internal sensitivity and low surface sensitivity.

B. A photosensitive element similar to (A) is prepared but with the hydrochloride salt of development accelerator V present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

C. A photosensitive element similar to (A) is prepared but with the hydrochloride salt of development accelerator VII present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

D. A photosensitive element similar to (A) is prepared but with the hydrochloride salt of development accelerator VIII present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

E. A photosensitive element similar to (A) is prepared but with the hydrochloride salt of development accelerator IX present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

F. A photosensitive element similar to (A) is prepared but with the hydrochloride salt of development accelerator X present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

G. A photosensitive element similar to (A) is prepared but with the hydrochloride salt of development accelerator XI present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

H. A photosensitive element similar to (A) is prepared but with the hydrochloride salt of development accelerator XII present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

I. A photosensitive element similar to (A) is prepared but with the hydrochloride salt of development accelerator XIV present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

J. A photosensitive element similar to (A) is prepared but with potassium 2-(2-octadecyl)-5-sulfonhydroquinone present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}. This sulfonated hydroquinone is generically described in U.S. Pat. No. 3,227,552.

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

1. pH-lowering layer of polyacrylic acid (325 mg./ft.^{2});
2. timing layer of cellulose acetate (56 mg./ft.^{2});
3. subbing layer of gelatin-cellulose nitrate;
4. mordant layer of copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride] (200 mg./ft.^{2}) and polyvinyl alcohol (200 mg./ft.^{2}).

Photosensitive elements A–J above 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 each 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	40.0 g.
piperidino hexose reductone	0.20 g.
5-methylbenzotriazole	0.05 g.
hydroxyethyl cellulose	30 g.
distilled water to	1000 ml.

After 60 seconds at about 240° C., the film units are separated. The maximum dye densities (Dmax) are then measured and are listed in Table 1.

TABLE 1

Photosensitive element	Development accelerator (HCl salt)	Dmax Red	Green	Blue
A	none (control)	0.28	0.64	1.48
B	V	2.22	2.24	1.68
C	VII	2.18	2.12	1.98
D	VIII	1.98	1.97	2.14
E	IX	2.12	2.12	2.08
F	X	1.69	1.90	2.18
G	XI	1.94	1.98	2.12
H	XII	2.10	2.10	2.10
I	XIV	2.00	2.20	1.20
J	*	2.20	2.20	1.72

*potassium 2-(2-octadecyl)-5-sulfohydroquinone

The above results indicate that use of a development accelerator in accordance with our invention significantly improves the Dmax in comparison with the control. Further, when compared with a prior-art compound, the blue Dmax obtained in accordance with our invention is generally higher while maintaining an acceptable red and green Dmax.

EXAMPLE 2

K. A photosensitive element is prepared similar to (A) of Example 1 except that layer 5 contains a blue-sensitive internal-image gelatin-silver chlorobromide emulsion (91 mg. gelatin/ft.^{2} and 100 mg. silver/ft.^{2}), yellow image transfer coupler α-pivaloyl-α-[4-(N-methyl-N-octadecylsulfamoyl)phenoxy[-4-sulfamoylacetanilide (40 mg./ft.^{2}) and 1-hydroxy-N-[α-(2,4-di-tert-amylphenoxy)-butyl]-2-naphthamide (20 mg./ft.^{2}).

L. A photosensitive element similar to (K) is prepared but with the hydrochloride salt of development accelerator I present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

M. A photosensitive element similar to (K) is prepared but with the hydrochloride salt of development accelerator II present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

N. A photosensitive element similar to (K) is prepared but with the hydrochloride salt of development accelerator III present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

O. A photosensitive element similar to (K) is prepared but with the hydrochloride salt of development accelerator IV present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

P. A photosensitive element similar to (K) is prepared but with the hydrochloride salt of development accelerator V present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

Q. A photosensitive element similar to (K) is prepared but with the hydrochloride salt of development accelerator VI present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

R. A photosensitive element similar to (K) is prepared but with the hydrochloride salt of development accelerator VII present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

S. A photosensitive element similar to (K) is prepared but with potassium 2-(2-octadecyl)-5-sulfohydroquinone present in layers 1, 3 and 5 at a concentration of 1 mg./ft.^{2}.

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

1. mordant layer of N-n-hexadecyl-N-ethylmorpholinium ethosulfate (150 mg./ft.^{2}), methyl-tri-n-dodecylammonium p-toluenesulfonate (23 mg./ft.^{2}) and gelatin (740 mg./ft.^{2}); and

2. gelatin overcoat (100 mg./ft.^{2}).

Photosensitive elements L-S above are exposed and processed exactly as in Example 1 except that the processing composition is the following:

sodium hydroxide	25.0 g.
4-amino-N-ethyl-N-β-hydroxyethyl-aniline 30.0 g.	
piperidino hexose reductone	0.20 g.
5-nitrobenzimidazole	0.24 g.
hydroxyethyl cellulose	30.0 g.
benzyl alcohol	10.0 g.
distilled water to	1000 ml.

The following results are obtained:

TABLE 2

Photosensitive element	Development accelerator HCl salt)	Dmax Red	Green	Blue
L	I	1.36	1.52	1.42
M	II	1.22	1.46	1.48
N	III	1.22	1.44	1.38
O	IV	0.96	1.44	1.58
P	V	0.42	1.26	1.52
Q	Vi	1.24	1.48	1.42
R	VII	1.36	1.56	1.42
S	*	0.96	1.36	1.48

*potassium 2-(2-octadecyl)-5-sulfohydroquinone

As in Example 1, the above results indicate that use of a development accelerator in accordance with our invention as compared with a prior-art compound gives better maximum dye densities in most instances in two of the three colors.

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.

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, direct-positive, 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 development accelerator in said photosensitive element comprising a 2-substituted aminomethyl-5-alkylhydroquinone or salt thereof.

2. The film unit of claim 1 wherein said photosensitive element comprises a support having thereon a direct-positive, 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 direct-positive, 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 direct-positive, blue-sensitive silver halide emulsion layer having associated therewith a yellow dye image-providing material com-

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

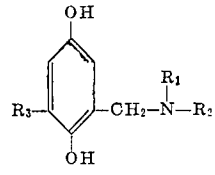
3. The film unit of claim 1 wherein said dye image-receiving layer is located in said photosensitive element between said support and the lowermost photosensitive silver halide emulsion layer.

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

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

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

7. The film unit of claim 1 wherein said 2-substituted aminomethyl-5-alkylhydroquinone has the following formula:



wherein R_3 is an alkyl group and R_1 and R_2 are each hydrogen, alkyl, alkenyl, aryl or may be taken together with the nitrogen to which they are attached to represent a heterocyclic ring.

8. The film unit of claim 7 wherein R_3 is an alkyl group of at least eight carbon atoms, R_1 is hydrogen or methyl and R_2 contains from two to 18 carbon atoms.

9. The film unit of claim 8 wherein said 2-substituted aminomethyl-5-alkylhydroquinone is 2-(N-allyl-N-methylamino-methyl)-5-octadecylhydroquinone, 2-(N-ethyl-N-methylamino-methyl)-5-octadecylhydroquinone or 2-morpholinomethyl-5-octadec-ylhydroquinone.

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 formulas:

$$DYE—LINK—(COUP—BALL)_n \quad \text{or} \quad BALL—LINK—(COUP—SOL)_n$$

wherein:

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

2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;

3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;

4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;

5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and

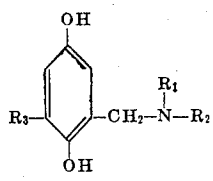
6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and *n* is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;

II. a dye image-receiving element comprising a support having thereon a dye 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 a development accelerator in said photosensitive element comprising a 2-substituted aminomethyl-5-alkylhydroquinone or salt thereof.

11. The film unit of claim 10 wherein said 2-substituted aminomethyl-5-alkylhydroquinone has the following formula:



wherein R_3 is an alkyl group and R_1 and R_2 are each hydrogen, alkyl, alkenyl, aryl or may be taken together with the nitrogen to which they are attached to represent a heterocyclic ring.

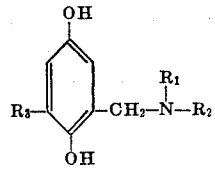
12. The film unit of claim 11 wherein R_3 is an alkyl group of at least eight carbon atoms, R_1 is hydrogen or methyl and R_2 contains from two to 18 carbon atoms.

13. The film unit of claim 12 wherein said 2-substituted aminomethyl-5-alkylhydroquinone is 2-(N-allyl-N-methylaminomethyl)-5-octadecylhydroquinone, 2-(N-ethyl-N-methyl-aminomethyl)-5-octadecylhydroquinone or 2-morpholinomethyl-5-octadecylhydroquinone.

14. A photosensitive element comprising a support having thereon at least one photosensitive, direct-positive, 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, said element containing a 2-substituted aminomethyl-5-alkylhydroquinone or salt thereof.

15. The photosensitive element of claim 14 wherein the photosensitive portion of said photosensitive element comprises a direct-positive, 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 direct-positive, 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 direct-positive, 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.

16. The photosensitive element of claim 14 wherein said 2-substituted aminomethyl-5-alkylhydroquinone has the following formula:



wherein R_3 is an alkyl group and R_1 and R_2 are each hydrogen, alkyl, alkenyl, aryl or may be taken together with the nitrogen to which they are attached to represent a heterocyclic ring.

17. The photosensitive element of claim 16 wherein R_3 is an alkyl group of at least eight carbon atoms, R_1 is hydrogen or methyl and R_2 contains from two to 18 carbon atoms.

18. The photosensitive element of claim 17 wherein said 2-substituted aminomethyl-5-alkylhydroquinone is 2-(N-allyl-N-methylaminomethyl-5-octadecylhydroquinone, 2-(N-ethyl-N-methylaminomethyl)-5-octadecylhydroquinone or 2-morpholino-methyl-5-octadecylhydroquinone.

19. 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 formulas:

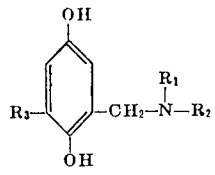
$$DYE—LINK—(COUP—BALL)_n \quad \text{or} \quad BALL—LINK—(COUP—SOL)_n$$

wherein:

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

said element containing a 2-substituted aminomethyl-5-alkylhy-droquinone or salt thereof.

20. The photosensitive element of claim 19 wherein said 2-substituted aminomethyl-5-alkylhydroquinone has the following formula:



wherein R_3 is an alkyl group and R_1 and R_2 are each hydrogen, alkyl, alkenyl, aryl or may be taken together with the nitrogen to which they are attached to represent a heterocyclic ring.

21. The photosensitive element of claim 20 wherein R_3 is an alkyl group of at least eight carbon atoms, R_1 is hydrogen or methyl and R_2 contains from two to 18 carbon atoms.

22. The photosensitive element of claim 21 wherein said 2-substituted aminomethyl-5-alkylhydroquinone is 2-(N-allyl-N-methylaminomethyl)-5-octadecylhydroquinone, 2-(N-ethyl-N-methylaminomethyl)-5-octadecylhydroquinone or 2-morpholino-methyl-5-octadecylhydroquinone.

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

A. imagewise-exposing a photosensitive element comprising a support having thereon at least one photosensitive, direct-positive, 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 development accelerator in said photosensitive element comprising a 2-substituted amino-methyl-5-alkylhydroquinone or salt thereof.

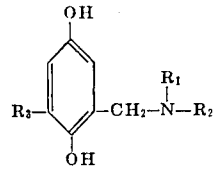
24. The process of claim 23 wherein said treatment step (B) is effected by:

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

b. positioning a rupturable container containing said alkaline processing composition between said exposed photosensitive element and said dye image-receiving layer; and

c. applying a compressive force to said container to effect a discharge of the container's contents between said outermost layer of said exposed photosensitive element and said dye image-receiving layer.

25. The process of claim 24 wherein said 2-substituted aminomethyl-5-alkylhydroquinone has the following formula:



wherein R_3 is an alkyl group and R_1 and R_2 are each hydrogen, alkyl, alkenyl, aryl or may be taken together with the nitrogen to which they are attached to represent a heterocyclic ring.

26. The process of claim 25 wherein R_3 is an alkyl group of at least eight carbon atoms, R_1 is hydrogen or methyl and R_2 contains from two to 18 carbon atoms.

27. The process of claim 26 wherein said 2-substituted aminomethyl-5-alkylhydroquinone is 2-(N-allyl-N-methylaminomethyl)-5-octadecylhydroquinone, 2-(N-ethyl-N-methyl-aminomethyl)-5-octadecylhydroquinone or 2-morpholinomethyl-5-octadecylhydroquinone.

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