3,698,897

DIFFUSION TRANSFER PROCESSES AND FILM UNITS COMPRISING COMPOUNDS WHICH ARE CLEAVABLE UPON OXIDATION IN ALKALI MEDIA TO PRODUCE DIFFUSIBLE DYES OR DYE PRECURSORS

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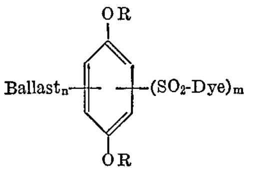
ABSTRACT OF THE DISCLOSURE

Color, diffusion transfer photographic elements, film units and processes are described which employ dye image-providing materials which are cleavable upon oxidation in an alkaline medium to release a dye or dye precursor which diffuses to a dye image-receiving layer. The compounds have the formula:



wherein R is H or a hydrolyzable entity, *n* is 1 to 3 and *m* is 1 to 3.

This invention relates to photography and more particularly to color, diffusion transfer photography employing dye image-providing materials which are cleavable upon oxidation in an alkaline medium.

Color, diffusion transfer processes of the prior art such as U.S. Pats. 2,983,606 and 3,222,169 generally involve the use of a photographic element comprising a support, at least one silver halide emulsion layer, and contained therein or contiguous thereto, a dye developer. A liquid processing composition is applied to the photosensitive element and permeates the emulsion to provide a solution of the dye developer substantially uniformly distributed therein. As the exposed silver halide emulsion is developed, the oxidation product of the dye developer is immobilized or precipitated in situ with the developed silver, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. This immobilization is apparently due, at least in part, to a change in the solubility charatceristics of the dye developer upon oxidation, and particularly as regards its solubility in alkaline solutions. At least part of this imagewise distribution of unoxidized dye developer is transferred to a superposed image-receiving layer to provide the transfer image.

In these prior art systems, the developer moiety of the dye developer is transferred with the dye to the image-receiving layer. In the absence of some further treatment, such as pH reduction with an acid, the developer moiety can undergo aerial oxidation which will have a substantial effect upon the stability to light of the resulting dye developer image. Accordingly, it would be highly desirable to provide a transfer system in which only the desired chemical entity, i.e., the dye, is transferred to the receiver.

In U.S. Pat. 3,245,789, dye developers are described which upon oxidation form an oxidation product which is more mobile and diffusible in the alkaline processing solution than is the dye developer. This patent does not disclose, however, the compounds of our invention which are cleavable upon oxidation in an alkaline medium.

It is therefore an object of this invention to provide photographic elements, film units and processes for producing a photographic transfer image in color in which only the dye portion of the dye image-providing material is transferred to the receiver.

It is another object of this invention to provide a photographic system wherein the dye portion of the dye image-providing material which is transferred to the receiver contains a solubilizing group as a result of cleavage in an alkaline solution.

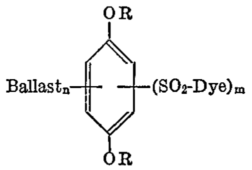
It is another object of this invention to provide photographic systems for producing a photographic transfer image in color which does not require a post-treatment in order to obtain light stability.

It is still a further object of this invention to provide photographic systems for producing photographic transfer images in color in which the dye image-receiving layer can either be located on a separate support or can be located integral with the photosensitive element.

These and other objects are achieved by our invention which is described hereinafter.

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 comprises:

(a) A photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer, each silver halide emulsion layer having associated therewith a dye image-providing material comprising a compound which is cleavable upon oxidation in an alkaline medium having the formula:



wherein:

(1) each R represents hydrogen or a hydrolyzable moiety;
(2) Ballast is a photographically inert organic ballasting radical of such molecular size and configuration as to render the cleavable compound nondiffusible during development in an alkaline processing composition;
(3) Dye is a dye or dye precursor;
(4) *n* is an integer of 1 to 3; and
(5) *m* is an integer of 1 to 3;

(b) A dye image-receiving layer; and

(c) A rupturable container containing an alkaline processing composition, said container being 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 a silver halide developing agent.

A photosensitive element according to our invention is set forth in (a) in the film unit described above.

A process for producing a photographic transfer image in color according to our invention comprises:

(a) Treating the above-described photosensitive element with an alkaline processing composition in the presence of said silver halide developing agent to effect development of each of the exposed silver halide emulsion layers, thereby oxidizing the developing agent;

(b) The oxidized developing agent thereby cross-oxidizing each cleavable compound to cause the compound to cleave at the SO_2 linkage, thus forming an imagewise distribution of diffusible dye or dye precursor containing the SO_2 moiety as a solubilizing group as a function of the imagewise exposure of each of the silver halide emulsion layers; and

(c) At least a portion of each of the imagewise distributions of diffusible dye or dye precursor containing said solubilizing group diffusing to a dye image-receiving layer to provide an image.

The photosensitive element in the above-described process can be treated with an alkaline processing composition to effect or initiate development in any manner. A preferred method for applying processing composition is by use of a rupturable container or pod which contains the composition. In general, the processing composition employed in our system contains the developing agent for development although the composition could also just be an alkaline solution where the developer is incorporated in the photosensitive element, in which case the alkaline solution serves to activate the incorporated developer.

The dye image-receiving layer in the above-described film unit can be located on a separate support adapted to be superposed on the photosensitive element after exposure thereof. Such image-receiving elements are generally disclosed, for example, in U.S. Pat. 3,362,819. A rupturable container is employed and is positioned in relation to the photosensitive element and the image-receiving element so that a compressive force applied to the container by pressure-applying members, such as would be found in a typical camera used for in-camera processing, will effect a discharge of the container's contents between the image-receiving element and the outermost layer of the photosensitive element. After processing, the dye image-receiving element is separated from the photosensitive element.

The dye image-receiving layer in the above-described film unit can also be located integral with the photosensitive element between the support and the lowermost photosensitive silver halide emulsion layer. A general format for integral receiver-negative photosensitive elements is disclosed in copending U.S. application Ser. No. 27,991 of Barr, Bush and Thomas filed Apr. 13, 1970 and now abandoned. In such an embodiment, the support for the photosensitive element is transparent and is coated with an image-receiving layer, a substantially opaque light-reflective layer, e.g., TiO_2, and then the photosensitive layer or layers 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 the 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 each exposed silver halide emulsion layer and dye images are formed as a function of development which diffuse to the image-receiving layer to provide a right-reading image which is viewed through the transparent support on the opaque reflecting layer background. For other details concerning the format of this particular integral film unit, reference is made to the above-mentioned Barr, Bush and Thomas U.S. application Ser. No. 27,991.

Another format for integral negative-receiver photosensitive elements in which the present invention can be employed is disclosed in Cole U.S. application Ser. No. 27,990 filed Apr. 13, 1970 and now abandoned. In this embodiment, the support for the photosensitive element is transparent and is coated with the image-receiving layer, a substantially opaque, light-reflective layer, the photosensitive layer or layers 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 throuhg 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 each silver halide layer and dye images are formed as a result of development which diffuse to the image-receiving layer to provide a right-reading image which is viewed through the transparent support on the opaque reflecting layer background. For further details concerning the format of this particular integral film unit, reference is made to the above-mentioned Cole U.S. application Ser. No. 27,990.

In the formua listed above for our compounds which are cleavable upon oxidation in an alkaline medium, R is preferably hydrogen, although it could be any hydrolyzable entity well-known to those skilled in the art, e.g., acetyl, mono-, di- or trichloroacetyl radicals, perfluoroacyl, pyruvyl, alkoxyacyl, nitrobenzoyl, cyanobenzoyl, sulfonyl, sulfinyl, etc.

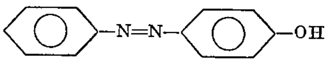
The nature of the ballast group in the formula for the compounds described above (Ballast) is not critical as long as it confers nondiffusibility to the compounds. Typical ballast groups include long-chain alkyl radicals linked directly or indirectly to the compound as well as aromatic radicals of the benzene and naphthalene series, etc. Useful ballast groups generally have at least 8 carbon atoms and may even comprise a Dye as defined below.

In addition to Ballast and SO_2-Dye, the benzene nucleus in the above formula may be substituted with groups such as the halogens, alkyl, aryl, alkoxy, aryloxy, nitro, amino, alkylamino, arylamino, amido, cyano, alkylmercapto, keto, carboalkoxy, etc.

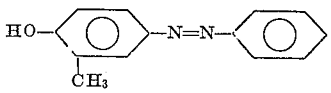
As previously mentioned, Dye in the above formula represents a dye or dye precursor. Such compounds are well-known to those skilled in the art and include dyes such as azo, azomethine, indoaniline, indophenol, anthraquinone, triarylmethane, alizarin, etc., and dye precursors such as a leuco dye, a "shifted" dye which shifts hypsochromically or bathochromically when subjected to a different environment such as a change in pH, reaction with a material to form a complex, etc., couplers such as a phenol, naphthol, indazolone, open-chain benzoyl acetanilide, pivalylacetanilide, malonamide, malonanilide, cyanoacetyl coumarone, pyrazolone, compounds described in U.S. Pat. 2,756,142, etc. Examples of such dyes include the following:

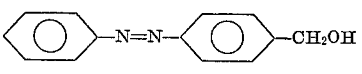
YELLOW DYES

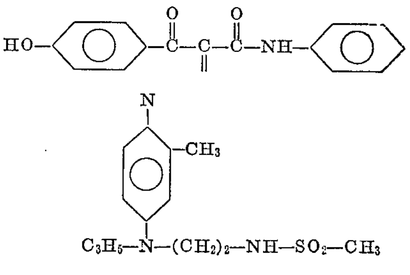
4-hydroxy azobenzene



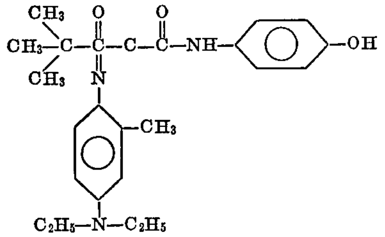
3-methyl-4-hydroxy azobenzene

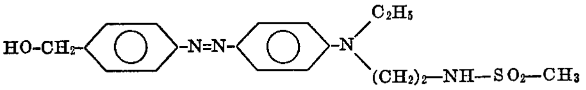




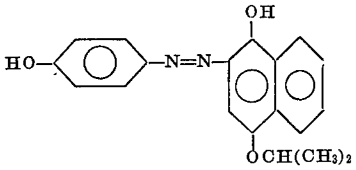


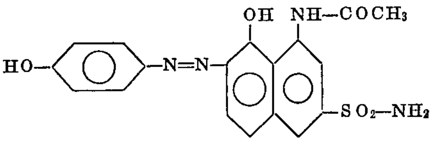
p-sulfhydryl azobenzene

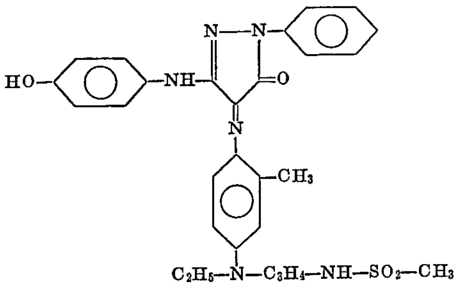




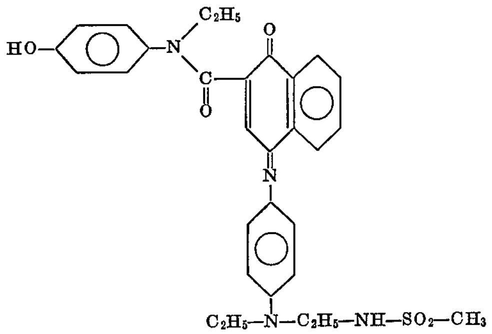
MAGENTA DYES

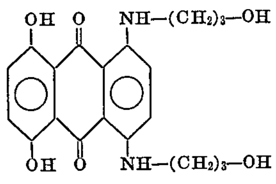






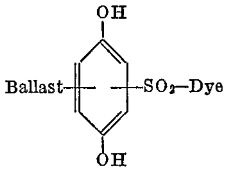
CYAN DYES





When dye precursors are employed in our process instead of dyes, they are converted to dyes by means well known to those skilled in the art either in the photosensitive element, in the processing composition or in the dye image-receiving layer to form a visible absorbing dye.

A preferred group of compounds which can be employed in our invention include those having the following formula:



wherein Dye and Ballast have the same definitions defined previously.

Compounds within this preferred formula include:

I: 3-[4-(4-phenylazobenzamido)phenylsulfonyl]-5-pentadecylhydroquinone

II: 2-{3-[4-(4-dimethylaminophenylazo)benzamido]phenylsulfonyl}-7-hexadecyloxynaphthhydroquinone

III: 2-{4-[4-(1-hydroxy-4-methoxy-2-naphthylazo)phenylacetamido]phenylsulfonyl}-5-pentadecylhydroquinone

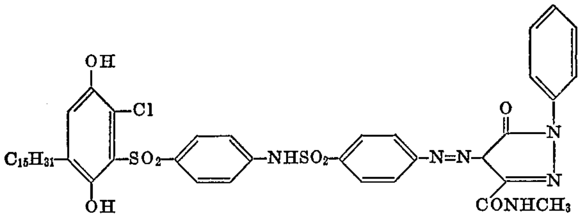
IV: 3-[4-(1-hydroxy-4-isopropoxy-2-naphthylazo)phenylsulfonyl]-5-pentadecylhydroquinone

V: 3-[4-(1-phenyl-3-methylcarbamoyl-4-pyrazolin-5-onylazo)-phenylsulfonyl]-5-pentadecylhydroquinone

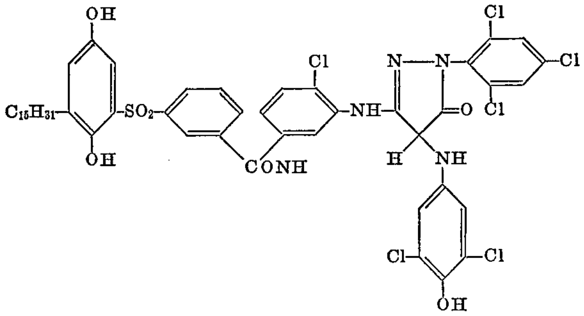
VI: 2-{3-{γ-{N-[1-(γ-methylsulfonamidopropylamino)-4-anthraquinonyl]amino}propylcarbamyl}phenylsulfonyl}-5-pentadecylhydroquinone

VII: Leuco shifted cyan dye-providing hydroquinone.—3-{3-[2-(3,5-dichloro-4-hydroxyphenylamino)-4-benzamido-5-hydroxyphenylcarbamoyl]benzenesulfonyl}-5-pentadecylhydroquinone

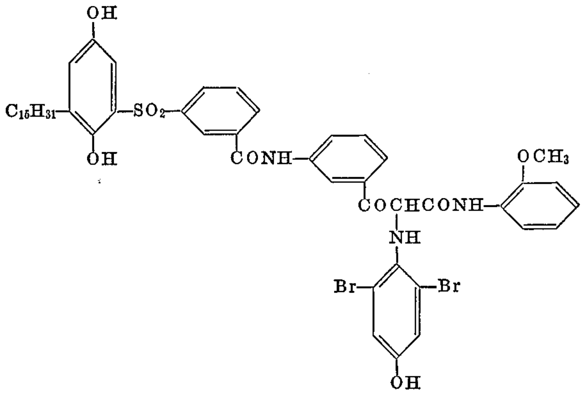
VII: 2-chloro-3-{4-[4-(1-phenyl-3-methylcarbamoyl-4-pyrazolin-5-onylazo)phenylsulfonamido]phenylsulfonyl}-5-pentadecylhydroquinone



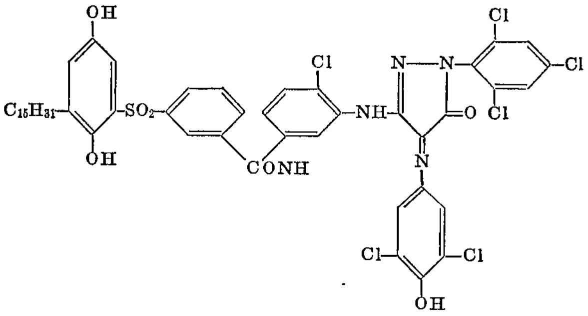
IX: Leuco shifted magenta dye-providing hydroquinone



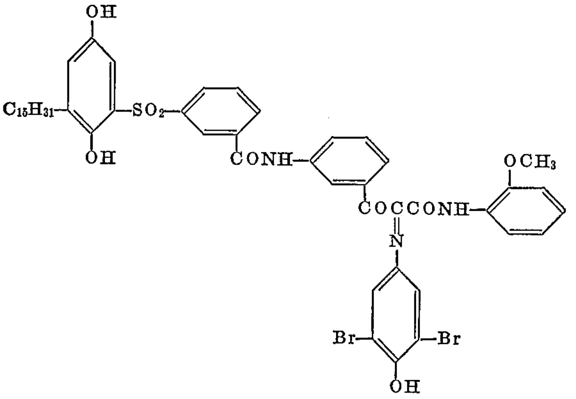
X: Leuco shifted yellow dye-providing hydroquinone



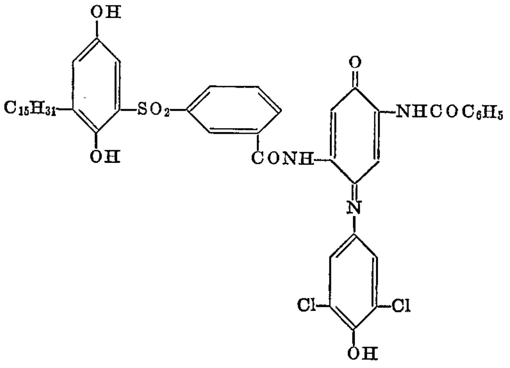
XI: Shifted magenta dye-providing hydroquinone



XII: Shifted yellow dye-providing hydroquinone



XIII: Shifter cyan dye-providing hydoquinone



Of the above compounds, especially good results are obtained with Compounds I, IV, V, VII and VIII.

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

The concentration of the cleavable compounds that are employed in the present invention may be varied over a

wide range depending upon the particular compound employed and the results which are desired. For example, cleavable dye image-providing compounds of the present invention may be coated in layers by using coating solutions containing between about 0.5 and about 8 percent by weight, of the dye image-providing compound distributed in a hydrophilic film-forming natural material or synthetic polymer, such as gelatin, polyvinyl alcohol, etc., which is adapted to be permeated by aqueous alkaline processing composition.

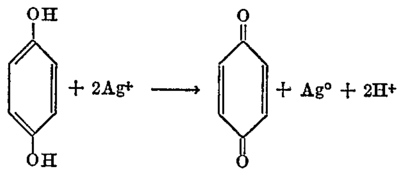
Any silver halide developing agent can be employed in our invention as long as it cross-oxidizes with the cleavable compounds described herein. The developer may be employed in the photosensitive element to be actuated by the alkaline processing composition. Specific examples of developers which can be employed in our invention include:

Hydroquinone
N-methylaminophenol
Phenidone
Dimezone
Aminophenols
N-N-diethyl-p-phenylenediamine
3-methyl-N,N-diethyl-p-phenylenediamine
3-methoxy-N-ethyl-N-ethoxy-p-phenylenediamine, etc.

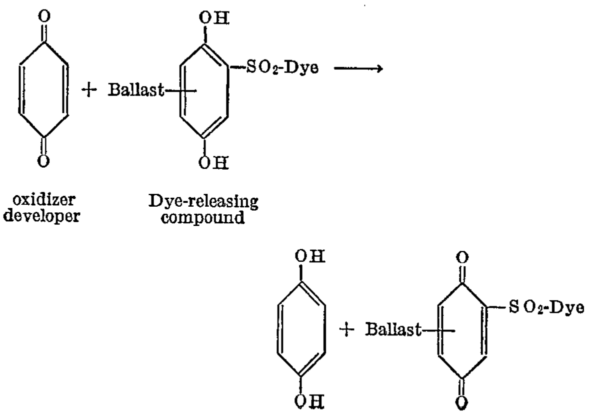
In addtion, we have found that the presence of sulfite ions in the processing composition enhances the cleavage reaction. Such sulfite ions can be conveniently employed in the processing composition in the form of their alkali metal salts, e.g., sodium sulfite, potassium sulfite, etc.

As was mentioned previously, the silver halide developer in our process becomes oxidized upon development and reduces silver halide to silver metal. The oxidized developer then cross-oxidizes the cleavable compound causing it to cleave at the SO_2 linkage, thus forming an imagewise distribution of diffusible dye or dye precursor containing the SO_2 solubilizing group which then diffuses to the receiving layer to provide the dye image. Although it is not intended to limit the present invention to any particular theory or reaction mechanism, it is believed that the following chemical reactions take place according to a particular process of the invention:

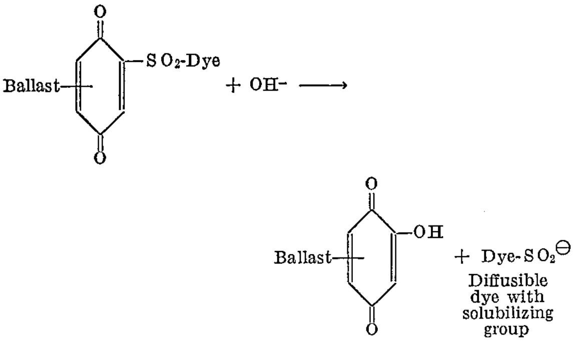
(1) Development of a latent image with hydroquinone, thereby oxiding it to a quinone



(2) Cross-oxidation step in which quinone is reduced and dye-releasing compound is oxidized



(3) Cleavage step under alkaline conditions to release a diffusible dye



In using the cleavable compounds according to our invention, the production of diffusible dye or dye precursor 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 a silver halide 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 on the dye image-receiving layer. 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 developing agent present in the film unit develops each of the silver halide emulsion layers in the unexposed areas (since the silver halide emulsions are direct-positive ones), thus causing the developing agent to become oxidized imagewise corresponding to the unexposed areas of the direct positive silver halide emulsion layers The oxidized developing agent then cross-oxidizes the cleavable compounds and the oxidized form of the compounds then undergoes a base-catalyzed elimination reaction to release the preformed dyes or the dye precursors imagewise 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 dyes or dye precursors containing an SO_2 solubilizing group as a result of cleavage diffuse to the image-receiving layer to form a positive image of the original subject. After being contacted by the alkaline processing composition, a pH-lowering layer in the film unit or image-receiving unit (if such a layer is needed) lowers the pH of the film unit or image-receiver to stabilize the image.

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. 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

	G.
Hydroquinone	15
Monomethyl-p-aminophenol sulfate	15
Sodium sulfite (desiccated)	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20

Water to make one liter.

DEVELOPER B

	G.
p-Hydroxyphenylglycine	10
Sodium carbonate	100

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, pp. 261–297. Typical methods for the preparation of solarizing emulsions are shown by Groves British Pat. 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. 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. 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. 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. 3,367,778; Illingsworth U.S. Pats. 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 in a convenient way to inject electrons into the silver halide grains. Suitable fogging agents include the hydrazines disclosed in Ives U.S. Pats. 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. 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.

Other embodiments in which our imaging chemistry can be employed include the techniques described in U.S. Pats. 3,227,550; 3,227,551; 3,227,552; and in British Pat. 904,364, page 19, lines 1–41, wherein our dye image-providing materials are substituted for the nondiffusible couplers described therein. For example, a film unit using development inhibitor-releasing couplers as described in U.S. Pat. 3,227,551 may be employed in conjunction with the dye image-providing materials described herein. In this method, however, the developing agent employed is restricted to one which oxidatively couples to release the inhibitor compounds. These developing agents are generally selected from the class of aromatic primary amino developing agents such as p-aminophenols or p-phenylenediamines.

Another embodiment of our invention uses the image-reversing technique disclosed in British Pat. 904,364, page 19, lines 1–41. In this system our cleavable compounds are used in combination with physical development nuclei in a nuclei layer contiguous to the photosensitive silver halide emulsion layer. The film unit contains a silver halide solvent, preferably in a rupturable container with the alkaline processing composition, and the photosensitive element contains an immobilizing coupler, which is capable of reacting with oxidized developer to form an immobile product. This embodiment also restricts the choice of developing agents to one which is reactive with the immobilizing coupler. Preferred compounds include the primary aromatic amines 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. 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. 2,526,632, issued Oct. 24, 1950; Sprague, U.S. Pat. 2,503,776, issued Apr. 11, 1950; Brooker et al., U.S. Pat. 2,493,748, issued Jan. 10, 1950; and Taber et al., U.S. Pat. 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 system 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, cadimum salts, and organic sulfonic acids as described in McFall et al., U.S. Pat. 2,933,390 issued Apr. 19, 1960 and Jones et al., U.S. Pat. 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. 2,222,264 issued Nov. 19, 1940; Illingsworth, U.S. Pat. 3,320,069 issued May 16, 1967; and McBride U.S. Pat. 3,271,157 issued Sept. 6, 1966. Surface-image emulsions can be used or internal-image emulsions can be used such as those described in Davey et al., U.S. Pat. 2,592,250 issued May 8, 1952; Porter et al., U.S. Pat. 3,206,313 issued Sept. 14, 1965; Berriman, U.S. Pat. 3,367,778 issued Feb. 6, 1968; and Bacon et al., U.S. Pat. 3,447,927 issued June 3, 1969. The emulsions may be regular-grain emulsions such as the type described in Klein and Moisar, J. Phot. Sci., vol. 12, No. 5, September/October, 1964, (pp. 242–251). Negative-type emulsions may be used or direct-positive emulsions may be used such as those described in Leermakers, U.S. Pat. 2,184,013 issued Dec. 19, 1939; Kendall et al., U.S. Pat. 2,541,472 issued Feb. 13, 1951; Berriman, U.S. Pat. 3,367,778 issued Feb. 6, 1968; Schouwenaars, British Pat. 723,019 issued Feb. 2, 1955; Illingsworth et al., French Pat. 1,520,821 issued Mar. 4, 1968; Illingsworth, U.S. Pat. 3,501,307 issued Mar. 17, 1970; Ives, U.S. Pat. 2,563,785 issued Aug. 7, 1951; Kuott et al., U.S. Pat. 2,456,953 issued Dec. 21, 1948; and Land, U.S. Pat. 2,861,885 issued Nov. 25, 1958.

The emulsions used with this invention may be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al., U.S. Pat. 1,623,499 issued Apr. 5, 1927; Waller et al., U.S. Pat. 2,399,083 issued Apr. 23, 1946; McVeigh, U.S. Pat. 3,297,447 issued Jan. 10, 1967; and Dunn, U.S. Pat. 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. 2,886,437 issued May 12, 1959; Dann et al., U.S. Pat. 3,046,134 issued July 24, 1962; Carroll et al., U.S. Pat. 2,944,900 issued July 12, 1960; and Goffe, U.S. Pat. 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. 2,131,038 issued Sept. 27, 1938; and Allen et al., U.S. Pat. 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper, U.S. Pat. 2,886,437 issued May 12, 1959; and Heimbach et al., U.S. Pat. 2,444,605 issued July 6, 1948; the mercury salts as described in Allen et al., U.S. Pat. 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al., U.S. Pat. 3,287,135 issued Nov. 22, 1966; the sulfocatechols described in Kennard et al., U.S. Pat. 3,236,652 issued Feb. 22, 1966; the oximes described in Carroll et al., British Pat. 623,448 issued May 18, 1949; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al., U.S. Pat. 2,403,927 issued July 16, 1946; Kennard et al., U.S. Pat. 3,266,897 issued Aug. 16, 1966;

and Luckey et al., U.S. Pat. 3,397,987 issued Aug 20, 1968; the polyvalent metal salts described in Jones, U.S. Pat. 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al., U.S. Pat. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al., U.S. Pat. 2,566,263 issued Aug. 28, 1951; and Yutzy et al., U.S. Pat. 2,597,915 isused May 27, 1952.

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. 3,421,892, or any of those disclosed in French Pat. 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; 3,121,001; 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 which can be employed include both naturally-occurring substances such as proteins, e.g., gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(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. 3,142,568 issued July 28, 1964; White, U.S. Pat. 3,193,386 issued July 6, 1965; Houck et al., U.S. Pat. 3,062,674 issued Nov. 6, 1962; Houck et al., U.S. Pat. 3,220,844 issued Nov. 30, 1965; Ream et al., U.S. Pat. 3,287,289 issued Nov. 22, 1966; and Dykstra, U.S. Pat. 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 facilities hardening or curing described in Smith, U.S. Pat. 3,488,708 issued Jan. 6, 1970, and those having recurring sulfobetaine units as described in Dykstra, Canadian Pat. 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. 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. 2,484,430 issued Oct. 11, 1949, and cetyl trimethylammonium bromide, etc. Effective mordanting compositions are also described in Whitmore, U.S. Pat. 3,271,148 and Bush, U.S. Pat. 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-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, 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. 3,362,819 or solid acids or metallic salts, e.g., zinc acetate, zinc sulfate, magnesium acetate, etc., as disclosed in U.S. Pat. 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 the practice of our invention over the pH-lowering 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. 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, cellulose esters, etc.

The alkaline processing composition employed in this invention is the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 12, and preferably containing a developing agent as described previously. The solution also preferably contains a viscosity-increasing compound such as a high molecular-weight polymer, e.g., a water-soluble ether inert to alkaline solutions such as hydroxyethyl cellulose or alkali metal salts of carboxymethyl cellulose such as sodium carboxymethy cellulose. A concentration of viscosity-increasing compound of about 1 to about 5% by weight of the processing composition is preferred which will impart thereto a viscosity of about 100 c.p.s. to about 200,000 c.p.s. 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 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, e.g., carbon black, nigrosine dyes, etc., may be added to it, or coated in a separate layer adjacent to the light-reflective layer.

The supports for the photographic elements of this invention can be any material as long as it does not deleteriously affect the photographic properties of the film unit and is dimensionally stable. Typical 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, 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. 2,600,831 issued June 17, 1952; amphoteric compounds such as those described in Ben-Ezra, U.S. Pat. 3,133,816 issued May 10, 1964; and water-soluble adducts of glycidal and an alkyl phenol such as those described in Olin Mathieson, British Pat. 1,022,878 issued Mar. 16, 1966; and Knox, U.S. Pat. 3,514,293 issued May 26, 1970.

The various layers, including the photographic layers, employed in the practice of this invention can contain light-absorbing materials and filter dyes such as those described in Sawdey, U.S. Pat. 3,253,921 issued May 31, 1966; Gaspar, U.S. Pat. 2,274,782 issued Mar. 3, 1942; Silberstein et al. U.S. Pat. 2,527,583 issued Oct. 31, 1950; and VanCampen, U.S. Pat. 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. 2,912,343 issued Nov. 10, 1959; McCrossen et al., U.S. Pat. 3,342,605 issued Sept. 19, 1967; Audran, U.S. Pat. 2,996,287 issued Aug. 15, 1961 and Johnson et al., U.S. Pat. 3,425,835 issued Feb. 4, 1969.

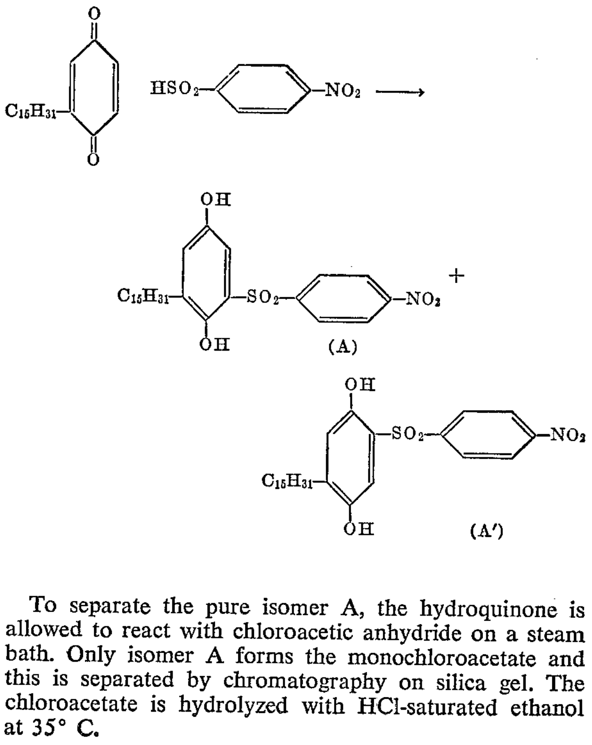
The photographic layers used in the practice of this invention may be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin, U.S. Pat. 2,681,294 issued June 25, 1954. If desired, two or more layers may be coated simultaneously by the procedures described in Russell, U.S. Pat. 2,761,791 issued Sept. 4, 1956; Hughes, U.S. Pat. 3,508,947 issued Apr. 18, 1970; and Wynn, British Pat. 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. 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. 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. 3,539,644 issued Nov. 10, 1970; active halogen compounds, epoxy compounds, aziridines, active olefines, isocyanates, carbodiimides, polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

The following examples further illustrate the invention.

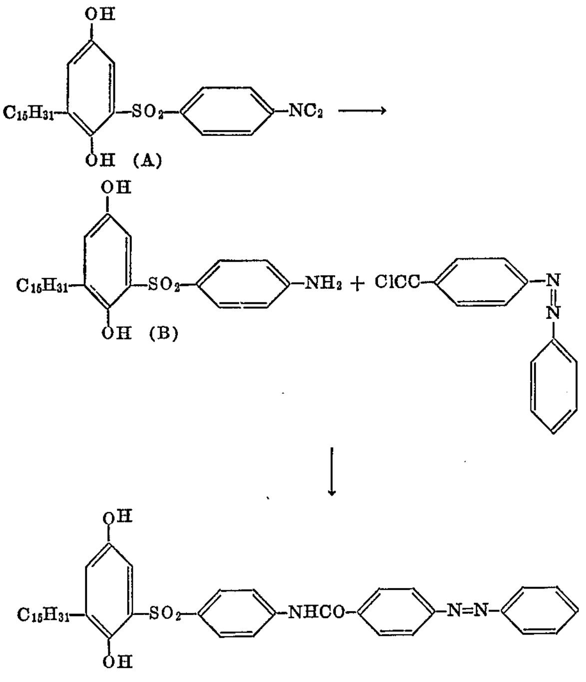
EXAMPLE 1

A mixture of 32 g. (0.1 mole) of n-pentadecylquinone and 34 g. (0.2 mole) of p-nitrobenzenesulfinic acid is stirred in 300 m. of tetrahydrofuran at ambient temperature for 20 hours. The mixture is concentrated to half its volume in vacuo and poured into 3 liters of water. The brown gum is washed with water several times until it solidifies to a brown, waxy solid which is mostly 3-(4-nitrophenylsulfonyl)-5-pentadecylhydroquinone (A, below) M.P. 80–95° C. The material is a mixture of isomers comprising about 80% of A and 20% of A':



To separate the pure isomer A, the hydroquinone is allowed to react with chloroacetic anhydride on a steam bath. Only isomer A forms the monochloroacetate and this is separated by chromatography on silica gel. The chloroacetate is hydrolyzed with HCl-saturated ethanol at 35° C.

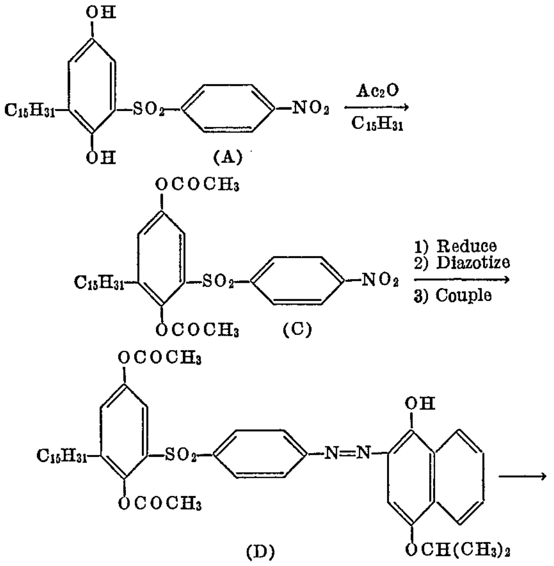
EXAMPLE 2.—PREPARATION OF COMPOUND I

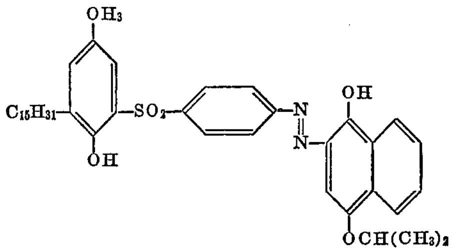


Compound I

A 4.0 g. portion of Compound A in 100 ml. of tetrahydrofuran is reduced over palladium on carbon at two atmospheres' hydrogen pressure in a Parr (Trademark) shaker. The solvent is removed in vacuo and the residual gum (B) is dissolved in 20 ml. of dry dioxane. To this are added 2.0 g. of 4-phenylazobenzoyl chloride followed by 2.0 ml. of quinoline. The mixture is stirred at ambient temperature for 24 hours, poured into water, and the resulting gum washed several times with water by decantation. The gum is dissolved in acetonitrile and a yellow solid crystallizes after scratching. The solid mixture is dissolved in chloroform and poured into a silica gel column and then developed with chloroform to remove certain impurities. The desired product is removed from the column with a mixture of 10% methanol-90% chloroform and recrystallized from chloroform to yield fine yellow plates of 3-[4-(4-phenylazobenzamido)phenylsulfonyl]-5-pentadecylhydroquinone (Compound I), M.P. 155–165° C.

EXAMPLE 3.—PREPARATION OF COMPOUND IV





Preparation of 3-(4-nitrophenylsulfonyl)-5-pentadecylhydroquinone diacetate (C)

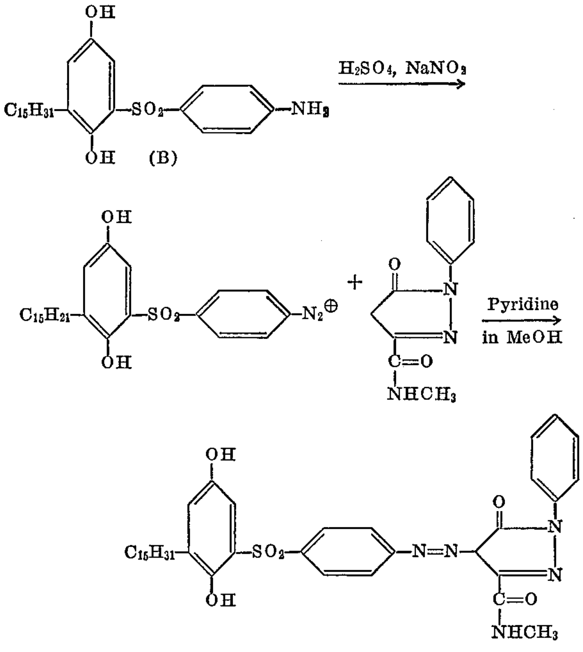
A 3.0 g. sample of Compound A is heated on a steam bath with a mixture of 10 ml. acetic anhydride and 1 drop of concentrated H_2SO_4. After 1 hour, the mixture is poured into 200 ml. water at 60° C., held at 60° C. for 5 minutes and then cooled. The supernatant liquid is removed by decantation and the residual gum is crystallized from a mixture of acetonitrile and ethanol to yield 2.9 g. of the diacetate, M.P. 77.5–78.5° C.

Preparation of 3-[4-(1-hydroxy-4-isopropoxy-2-naphthylazo)phenylsulfonyl]-5-pentadecylhydroquinone diacetate (D)

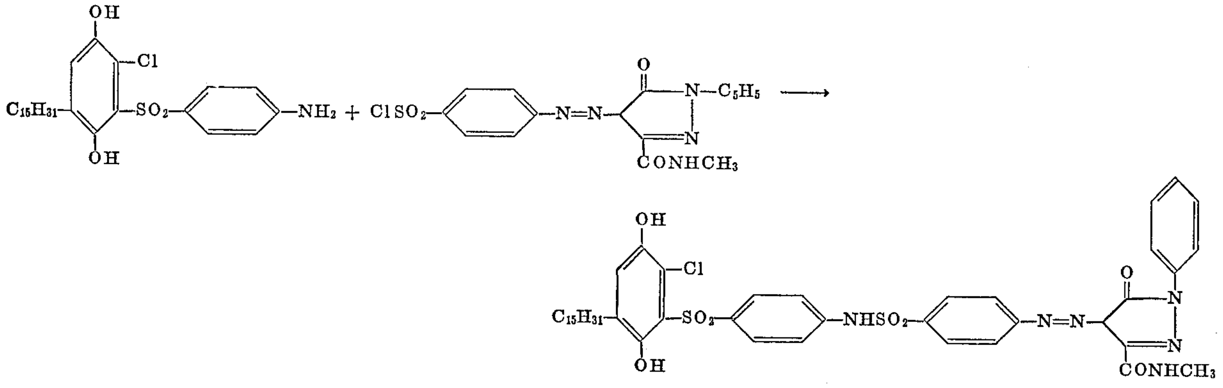
Compound C (2.8 g.) is reduced in 100 ml. tetrahydrofuran over palladium on carbon. After filtering off the catalyst and removing the solvent in vacuo, a gum remains. This is dissolved at 15° C. in 40 ml. of acetate acid to which 1.3 ml. H_2SO_4 and 0.35 g. $NaNO_2$ are added. After stirring for 15 minutes, another 1.0 ml. H_2SO_4, followed by 0.1 g. $NaNO_2$ and 5 ml. chloroform, is added and dissolution results soon thereafter. The solution is added at 0° C. to a stirred solution of 1.1 g. of 4-isopropoxynaphthol in 70 ml. of pyridine mixed with 70 ml. of methanol. The mixture is stirred overnight and 30 ml. of water are added to precipitate a magenta dye which, after recrystallization from methanol, yields 0.6 g. of product, M.P. 149–151° C.

Compound D (0.5 g.) is hydrolyzed under nitrogen in a mixture of 15 ml. ethanol, 50 ml. H_2O and 1 g. of 50% NaOH. After 35 minutes at 65° C., it is acidified with acetic acid, collected and recrystallized from ethanol to yield 0.25 g. of Compound IV, M.P. 159–163° C.

EXAMPLE 4.—PREPARATION OF COMPOUND V



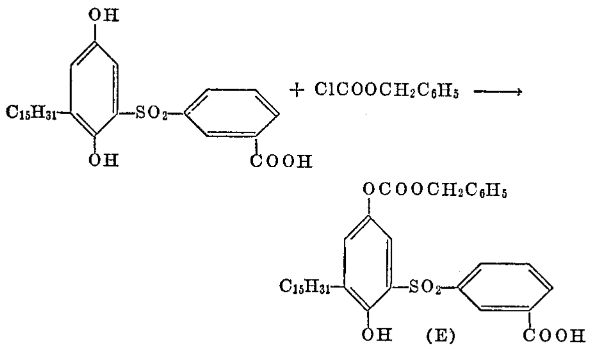
To a solution of 20.0 g. (0.042 mol.) of Compound B in 20 ml. of DMF are added 400 ml. of glacial acetic acid and 400 ml. of propionic acid. The mixture is cooled to 0° C. in an ice-water bath, 12.0 g. concentrated H_2SO_4 are added, followed by the dropwise addition of 2.6 g. (0.038 mol.) sodium nitrite dissolved in 5 ml. water. The mixture is immediately poured with stirring into a solution (at 0° C.) of 9.1 g. (0.042 mol.) of 1-phenyl-3-methylcarbamoyl-5-pyrazolone in 400 ml. pyridine and 800 ml. methanol. The solution is evaporated to about 200 ml. and poured into 1 liter of cold water with vigorous stirring. The yellow solid is filtered and dried. The crude product is dissolved in 50 ml. acetone and allowed to stand at room temperature. A yellow, crystalline product, 16 g. (54%), is obtained. The product is recrystallized from ethyl acetate to yield Compound V, M.P. 155–157° C.



In 50 ml. dry dioxan are mixed 2.3 g. (4.6 mmols.) of 2-chloro-3-(4-aminophenylsulfonyl)-5-pentadecylhydroquinone, 2.0 g. (5.0 mmols.) of 4-(1 phenyl-3-methylcarbamoyl-4-pyrazoline-5-onlyazo)phenylsulfonyl chloride and 0.4 g. (5.1 mmols.) of pyridine. The mixture is refluxed for 18 hours, then poured into cold water. The resulting solid is filtered, dried, dissolved in chloroform and the dye isolated by chromatography on silica gel. One crystallization from ethanol yields 1.5 g. M.P. 171–173° C.

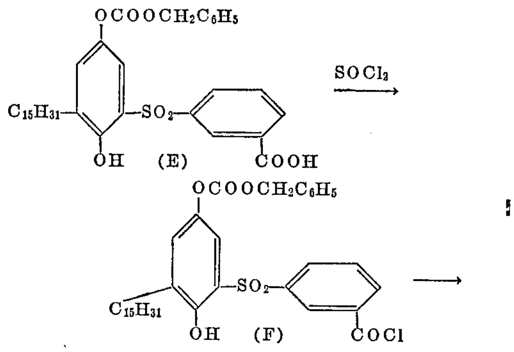
EXAMPLE 6.—PREPARATION OF COMPOUND VII

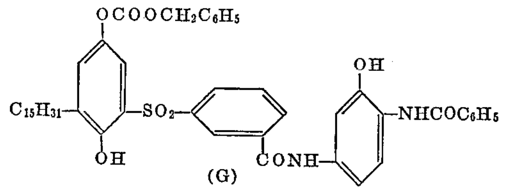
Preparation of 3-(3-carboxyphenylsulfonyl)-5-pentadecylhydroquinone benzylcarbonate (E)



To a solution of 3.3 g. of sodium hydroxide in 270 ml. H_2O and 220 ml. dioxane under nitrogen are added 10 g. (0.03 mol.) of 3-(3-carboxyphenylsulfonyl)-5-pentadecylhydroquinone in 50 ml. of dioxane. This solution is chilled to 3° C. and 10 g. of benzylchloroformate (0.06 mol.) are dropped in with stirring over 5 minutes. After 90 minutes at 0° C., the solution is acidified with HCl, extracted with chloroform and the extracts washed with water. The chloroform solution is dried ($MgSO_4$) and the desired product separated by chromatography on silica gel.

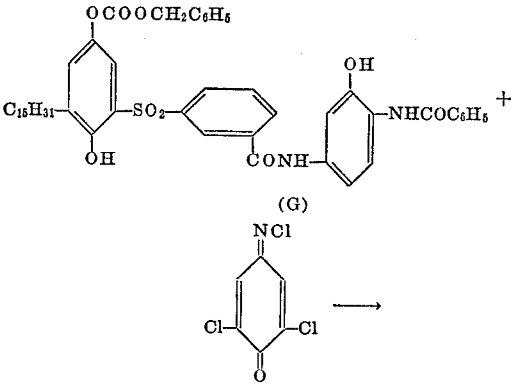
Preparation of 3-[3-(3-hydroxy-4-benzamidophenylcarbamoyl)phenylsulfonyl]-5-pentadecylhydroquinone benzylcarbonate (G)

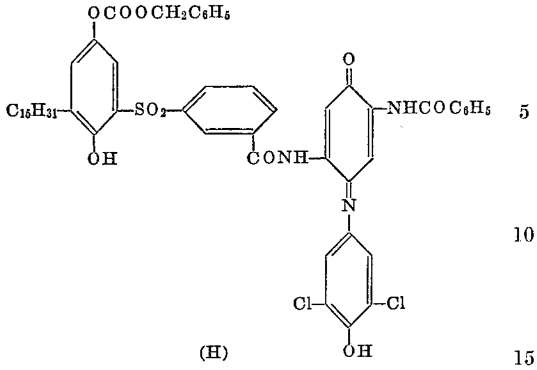




A 5-g. portion of Compound E in 10 ml. of thionyl chloride and 30 ml. of chloroform is refluxed for 1 hour and the solvents removed in vacuo. The resulting gum (Compound F) is dissolved in 30 ml. dry dioxane and then 5 g. of 2-benzamido-5-aminophenol and 4 g. of quinoline are added. The mixture is stirred at ambient temperature for 1 hour and then heated in the steam bath for 15 minutes. It is poured into ice water, the resulting gum washed by decantation and then dissolved in a hexane-chloroform mixture. After drying ($MgSO_4$), a gummy solid forms slowly. Two recrystallizations from an ethanol-methanol mixture yields 6 g. of solid, Compound G, M.P. 123–133° C.

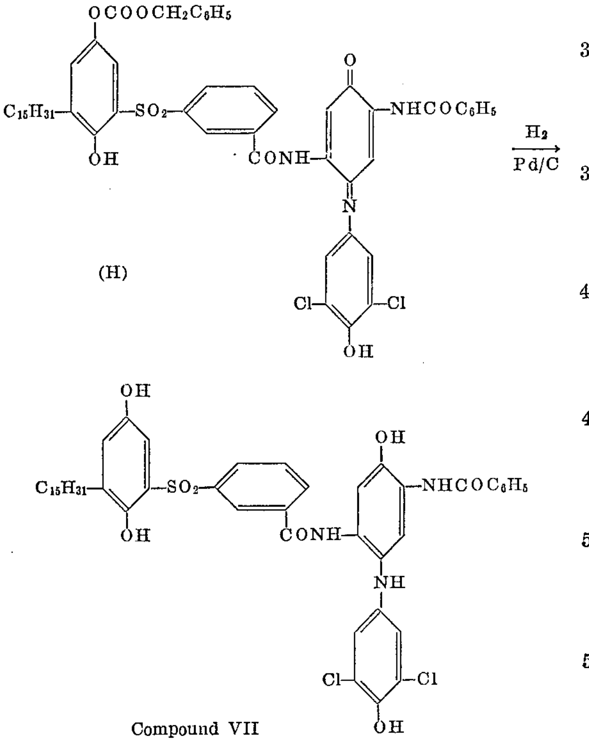
Preparation of 3-{3-[3-oxo-4-benzamido-6-(4-hydroxy-3,5-dichlorophenylimino)cyclohexadienylcarbamoyl]phenylsulfonyl}-5-pentadecylhydroquinone benzylcarbonate (H)





(H)

A 3.2-g. (3.8 mmol.) portion of Compound G is mixed in 300 ml. tetrahydrofuran with 0.8 g. (3.8 mmol.) of 2,6-dichloro-4-N-chloroquinoneimine at room temperature. To this is added with stirring a solution of 2.0 g. of sodium bicarbonate in 300 ml. of water and 100 ml. of ethanol. After stirring at ambient temperature for 1 hour, the solution is acidified with acetic acid and diluted with 800 ml. water. The mixture is extracted with chloroform, the extracts washed with water and dried ($MgSO_4$). The desired dye is separated by chromatography on silica gel and recrystallized from acetonitrile to yield 1.6 g. of Compound H, M.P. 138–148° C.



(H)

Compound VII

A 3.4-g. sample of Compound H is reduced over palladium on carbon in a mixture of 100 ml. ethanol, 100 ml. tetrahydrofuran and 1 ml. acetic acid. The catalyst is filtered off and the solvents removed in vacuo. The resulting gum is crystallized from acetonitrile to yield 1.5 g. of grayish yellow solid of Compound VII, M.P. 167–175° C.

EXAMPLE 7

A single-layer, light-sensitive element is prepared by dissolving 0.3 g. of Compound I in 0.6 ml. of diethyl lauramide and 3.0 ml. of 2-methyltetrahydrofuran. The solution is dispersed in 15.5 ml. of aqueous gelatin with a colloid mill. One ml. of tri-isopropyl naphthalene sulfonate as a 5% solution is added to aid in dispersion. To this is added 3 ml. of a gelatin-silver bromide emulsion and 1.0 ml. of a 7½% solution of the spreading agent saponin. The volume of the mixture is adjusted with water and 10% gelatin and coated on a support such that about 32×10^{-4} moles/ft.^{2} of silver is present and there are 6 moles of silver coated for every 1 mole of Compound I.

A sample of the photosensitive element is exposed to a graduated-density multicolor test object. A processing composition comprising Phenidone (0.25 g./l.), NaOH (1 normal), Na_2SO_3 (25 g./l.) and hydroxyethylcellulose (30 g./l.) is employed in a pod and is spread between the exposed surface of the photosensitive element and a superposed dye image-receiving element comprising a support coated with 700 mg./ft.^{2} of gelatin and 150 mg./ft.^{2} of the mordant N-n-octadecyl-tri-butylammonium bromide, by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers.

After 60 seconds at about 24° C., the film unit is separated. A negative yellow dye image is observed on the dye image-receiving sheet.

EXAMPLE 8

A photosensitive element is prepared by coating on an opaque cellulose acetate film support a negative-working gelatin-silver chlorobromide emulsion (150 mg. gelatin/ft.^{2} and 60 mg. silver/ft.^{2}) and magenta cleavable Compound IV, 3-[4-(1-hydroxy-4-isopropoxy-2-naphthylazo) phenylsulfonyl]-5-pentadecylhydroquinone (60 mg./ft.^{2}).

A dye image-receiving element is prepared by coating an N-n-hexadecyl-N-morpholinium ethosulfate/methyl-tri-n-dodecylammonium p-toluenesulfonate coacervate mordant dispersion of the type described in U.S. Pat. 3,271,147 of Bush issued Sept. 6, 1966, on an opaque support.

A sample of the photosensitive element is 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 the superposed dye image-receiving element by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers:

	G.
Sodium hydroxide	40
Sodium sulfite	20
Hydroxyethylcellulose	25
Phenidone	1.5

Water to 1000 ml.

After 60 seconds at about 25° C., the dye image-receiving element is separated from the "negative" element. A negative, magenta dye image is observed on the dye image-receiving element.

EXAMPLE 9

The procedure of Example 8 is repeated except that the processing composition does not contain Phenidone. No visible dye image in the receiving element is obtained and no visible silver development takes place in the "negative" element. This example illustrates that the cleavable compounds of our invention are incapable of development themselves and require a separate silver halide developing agent in the system.

EXAMPLE 10

A photosensitive element is prepared by coating on an opaque cellulose acetate film support a negative-working gelatin-silver chlorobromide emulsion (150 mg. gelatin/ft.^{2} and 87 mg. silver/ft.^{2}) and yellow cleavable Compound V, 3-[4-(1-phenyl-3-methylcarbamoyl-4-pyrazolin-5-onylazo)phenylsulfonyl]-5-pentadecylhydroquinone (93.5 mg./ft.^{2}).

This element is exposed and processed as in Example 8 to obtain a negative, yellow dye image on the dye image-receiving element.

EXAMPLE 11

The procedure of Example 10 is repeated except that the processing composition does not contain Phenidone. No visible dye image in the receiving element is obtained and no visible silver development takes place in the "negative" element. This example illustrates that the cleavable compounds of our invention are incapable of development themselves and require a separate silver halide developing agent in the system.

EXAMPLE 12

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, negative-working, gelatin-silver chlorobromide emulsion (150 mg. gelatin/ft.^{2} and 87 mg. silver/ft.^{2}) and yellow cleavable Compound V, 3-[4-(1-phenyl - 3 - methylcarbamoyl - 4-pyrazolin-5-onylazo) phenylsulfonyl]-5-pentadecylhydroquinone (93.5 mg./ft.^{2});

(2) an interlayer of gelatin (80 mg./ft.^{2}), Phenidone (10 mg./ft.^{2}) (incorporated developing agent), 2,5-di-tert-octylhydroquinone (20 mg./ft.^{2}) (oxidized color developer scavenger) and yellow filter dye 1-(2,4,6-trichlorophenyl - 3 - {3-[α-(2,4-di-tert-amylphenoxy)acetamido]benzamido} - 4-(4-methoxyphenylazo)-5-pyrazolone (75 mg./ft.^{2}); and

(3) blue-sensitive, negative-working, gelatin-silver chlorobromide emulsion (150 mg./gelatin/ft.^{2} and 60 mg. silver/ft.^{2}) and magenta cleavable Compound IV, 3-[4-(1 - hydroxy - 4 - isopropoxy-2-naphthylazo)phenylsulfonyl]-5-pentadecylhydroquinone (60 mg./ft.^{2}).

A sample of the photosensitive element is 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 a superposed dye image-receiving element similar to that of Example 8 by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers:

	G.
Sodium hydroxide	20
Sodium sulfite	14
Hydroxyethylcellulose	25
Potassium bromide	10
Water to 1 l.	

(No developing agent is necessary in the processing composition since it is incorporated in the photosensitive element.) After 60 seconds at about 25° C., the dye image-receiving element is separated from the "negative" element. A well-defined, negative, two-color magenta-yellow reproduction of the test object is observed on the dye image-receiving element.

EXAMPLE 13

A photosensitive element is prepared by coating on an opaque cellulose acetate film support: (1) a negative-working gelatin-silver bromide emulsion (300 mg. gelatin/ft.^{2} and 100 mg. silver/ft.^{2}) and cyan dye-providing Compound VII (90 mg./ft.^{2}) (this compound is colorless in this state) and (2) gelatin overcoat (80 mg./ft.^{2}).

A dye image-receiving element is prepared as in Example 8.

A sample of the photosensitive element is exposed and processed as in Example 8 employing the following processing composition: NaOH (1 normal), Na_2SO_3 (20 g./l.), hydroxyethylcellulose (25 g./l.) and N-methyl-p-aminophenol (0.9 g./l.).

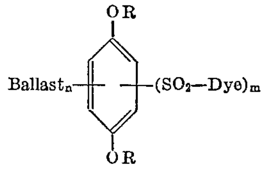
After 60 seconds at 24° C., the film unit is separated. A negative cyan dye image is observed on the dye image-receiving sheet.

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. 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 compound which is cleavable upon oxidation in an alkaline medium having the formula:



wherein:

(1) each R represents hydrogen or a hydrolyzable moiety;

(2) Ballast is a photographically inert organic ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline processing composition;

(3) Dye is a dye or dye precursor;

(4) *n* is an integer of 1 to 3; and

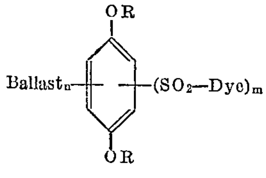
(5) *m* is an integer of 1 to 3.

2. The photosensitive element of claim **1** wherein R is H, *n* is 1 and *m* is 1.

3. The photosensitive element of claim **1** wherein said compound which is cleavable upon oxidation in an alkaline medium is

3-[4-(4-phenylazobenzamido)phenylsulfonyl]-5-pentadecylhydroquinone;
3-[4-(1-hydroxy-4-isopropoxy-2-naphthylazo)phenylsulfonyl]-5-pentadecylhydroquinone;
3-[4-(1-phenyl-3-methylcarbamoyl-4-pyrazolin-5-onylazo)phenylsulfonyl]-5-pentadecylhydroquinone;
3-{3-[2-(3,5-dichloro-4-hydroxyphenylamino)-4-benzamido-5-hydroxyphenylcarbamoyl]benzenesulfonyl}-5-pentadecylhydroquinone; or
2-chloro-3-{4-[4-(1-phenyl-3-methylcarbamoyl-4-pyrazolin-5-onylazo)phenylsulfonamido]phenylsulfonyl}-5-pentadecylhydroquinone.

4. A photosensitive element comprising a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a cyan dye image-providing material, a green-sensitive silver halide emulsion layer having associated therewith a magenta dye image-providing material, and a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye image-providing material, at least one of said dye image-providing materials being a compound which is cleavable upon oxidation in an alkaline medium having the formula:



wherein:

(1) each R represents hydrogen or a hydrolyzable moiety;

(2) Ballast is a photographically inert organic ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline processing composition;

(3) Dye is a dye or dye precursor;

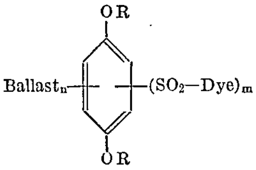
(4) *n* is an integer of 1 to 3; and

(5) *m* is an integer of 1 to 3.

5. The photosensitive element of claim **4** wherein R is H, *n* is 1 and *m* is 1.

6. 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 compound which is cleavable upon oxidation in an alkaline medium having the formula:



wherein:

(1) each R represent hydrogen or a hydrolyzable moiety;

(2) Ballast is a photographically inert organic ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline processing composition;

(3) Dye is a dye or dye precursor;

(4) *n* is an integer of 1 to 3; and

(5) *m* is an integer of 1 to 3;

(b) a dye image-receiving layer; and

(c) a rupturable container containing an alkaline processing composition, said container being 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 a silver halide developing agent.

7. The film unit of claim **6** wherein R is H, *n* is 1 and *m* is 1.

8. The film unit of claim **6** wherein said compound which is cleavable upon oxidation in an alkaline medium is

3-[4-(4-phenylazobenzamido)phenylsulfonyl]-5-pentadecylhydroquinone;

3-[4-(1-hydroxy-4-isopropoxy-2-naphthylazo)phenylsulfonyl]-5-pentadecylhydroquinone;

3-[4-(1-phenyl-3-methylcarbamoyl-4-pyrazolin-5-onylazo)phenylsulfonyl]-5-pentadecylhydroquinone;

3-{3-[2-(3,5-dichloro-4-hydroxyphenylamino)-4-benzamido-5-hydroxyphenylcarbamoyl]benzenesulfonyl}-5-pentadecylhydroquinone; or

2-chloro-3-{4-[4-(1-phenyl-3-methylcarbamoyl-4-pyrazolin-5-onylazo)phenylsulfonamido]phenylsulfonyl}-5-pentadecylhydroquinone.

9. The film unit of claim **6** wherein said dye image-receiving layer is located in said photosensitive element between said support and the lowermost photosensitive silver halide emulsion layer.

10. The film unit of claim **6** 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.

11. The film unit of claim **10** 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.

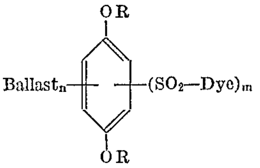
12. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

(a) a photosensitive element comprising a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a cyan dye image-providing material, a green-sensitive sliver halide emulsion layer having associated therewith a magenta dye image-providing material, and a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye image-providing material;

(b) a dye image-receiving layer; and

(c) a rupturable container containing an alkaline processing composition, said rupturable container being 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 a silver halide developing agent; at least one of said dye image-providing materials being a compound which is cleavable upon oxidation in an alkaline medium having the formula:



wherein:

(1) each R represents hydrogen or a hydrolyzable moiety;

(2) Ballast is a photographically inert organic ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline processing composition;

(3) Dye is a dye or dye precursor;

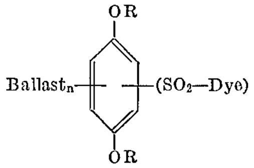
(4) *n* is an integer of 1 to 3; and

(5) *m* is an integer of 1 to 3.

13. The photographic film unit of claim **12** wherein R is H, *n* is 1 and *m* is 1 and said developing agent is contained in said rupturable container.

14. A process for producing a photographic transfer image in color 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 dye image-providing material comprising a compound which is cleavable upon oxidation in an alkaline medium having the formula:



wherein:

(1) each R represents hydrogen or a hydrolyzable moiety;

(2) Ballast is a photographically inert organic ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline processing composition;

(3) Dye is a dye or dye precursor;

(4) *n* is an integer of 1 to 3;

(5) *m* is an integer of 1 to 3;

(b) treating said photosensitive element with an alkaline processing composition in the presence of a silver halide developing agent to effect development of each of said exposed silver halide emulsion layers, thereby oxidizing said developing agent;

(c) said oxidized developing agent thereby cross-oxidizing each said cleavable compound to cause said compound to cleave at the SO_2 linkage, thus forming an imagewise distribution of diffusible dye or dye precursor containing the SO_2 moiety as a solubilizing group as a function of said imagewise exposure of each of said silver halide emulsion layers; and

(d) at least a portion of each of said imagewise distributions of diffusible dye or dye precursor containing said solubilizing group diffusing to a dye image-receiving layer to provide said transfer image.

15. The process of claim **14** 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 an alkaline possessing composition between said exposed photosensitive element and said dye image-receiving layer, said alkaline processing composition containing said developing agent; and

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

16. The process of claim **14** wherein R is H, *n* is 1 and *m* is 1.

17. The process of claim **14** wherein said compound which is cleavable upon oxidation in an alkaline medium is

3-[4-(4-phenylazobenzamido)phenylsulfonyl]-5-pentadecylhydroquinone;

3-[4-(1-hydroxy-4-isopropoxy-2-naphthylazo)phenylsulfonyl]-5-pentadecylhydroquinone;

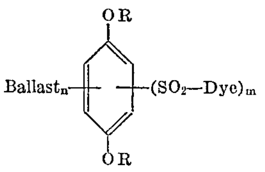
3-[4-(1-phenyl-3-methylcarbamoyl-4-pyrazolin-5-onylazo)phenylsulfonyl]-5-pentadecylhydroquinone;

3-{3-[2-(3,5-dichloro-4-hydroxyphenylamino)-4-benzamido-5-hydroxyphenylcarbamoyl]benzenesulfonyl}-5-pentadecylhydroquinone; or

2-chloro-3-{4-[4-(1-phenyl-3-methylcarbamoyl-4-pyrazolin-5-onylazo)phenylsulfonamido]phenylsulfonyl}-5-pentadecylhydroquinone.

18. A process for producing a photographic transfer image in color comprising:

(a) imagewise-exposing a photosensitive element comprising a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a cyan dye image-providing material, a green-sensitive silver halide emulsion layer having associated therewith a magenta dye image-providing material, and a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye image-provindg material, at least one of said dye image-providing materials comprising a compound which is cleavable upon oxidation in an alkaline medium having the formula:



wherein:

(1) each R represents hydrogen or a hydrolyzable entity;

(2) Ballast is a photographically inert organic ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline processing composition;

(3) Dye is a dye or dye precursor;

(4) *n* is an integer of 1 to 3; and

(5) *m* is an integer of 1 to 3;

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

(c) positioning a rupturable container containing an alkaline processing composition comprising a silver halide developing agent between said exposed photosensitive element and said dye image-receiving layer;

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

(e) thereby effecting development of each of said exposed silver halide emulsion layers, thereby oxidizing said silver halide developing agent;

(f) said oxidized developing agent cross-oxidizing each said cleavable compound to cause said compound to cleave at the SO_2 linkage, thus forming an imagewise distribution of diffusible dye or dye precursor containing the SO_2 moiety as a solubilizing group as a function of said imagewise exposure of each of said silver halide emulsion layers;

(g) at least a portion of each of said imagewise distributions of diffusible dye or dye precursor containing said solubilizing group diffusing to said dye image-receiving layer to provide said transfer image; and

(h) separating said photosensitive element from said dye image-receiving layer coated on its said support.

19. The process of claim **18** wherein R is H, *n* is 1 and *m* is 1.

20. A process for producing a photographic transfer image in color comprising:

(A) imagewise-exposing a photosensitive element comprising a transparent support having thereon the following layers in sequence:

(a) a dye image-receiving layer;

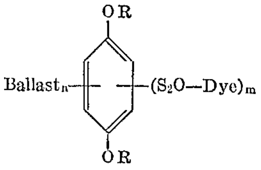
(b) an alkaline solution-permeable, substantially opaque light-reflective layer;

(c) a red-sensitive sliver halide emulsion layer having associated therewith a cyan dye image-providing material;

(d) a green-sensitive silver halide emulsion layer having associated therewith a magenta dye image-providing material; and

(e) a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye image-providing material;

at least one of said dye image-providing materials comprising a compound which is cleavable upon oxidation in an alkaline medium having the formula:



wherein:

(1) each R represents hydrogen or a hydrolyzable entity;

(2) Ballast is a photographically inert organic ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline processing composition;

(3) Dye represents a dye or dye precursor;

(4) *n* is an integer of 1 to 3; and

(5) *m* is an integer of 1 to 3;

(B) developing each said exposed silver halide emulsion layer with a silver halide developing agent thereby causing said developing agent to become oxidized;

(C) said oxidized developing agent thereby cross-oxidizing each said cleavable compound to cause said compound to cleave at the SO_2 linkage, thus forming an imagewise distribution of diffusible dye or dye precursor containing the SO_2 moiety as a solubilizing group as a function of said imagewise exposure of each of said silver halide emulsion layers; and

(D) at least a portion of each of said imagewise distributions of diffusible dye or dye precursor containing said solubilizing group diffusing to said dye image-receiving layer to provide said transfer image viewable through said transparent support.

21. The process of claim **20** wherein R is H, *n* is 1 and *m* is 1.

References Cited

UNITED STATES PATENTS

3,364,022	1/1968	Barr	96—3

JESSE T. BROWN, Primary Examiner

A. T. SURO PICÓ, Assistant Examiner

U.S. Cl. X.R.

96—29, 74, 76 C, 77