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Patented Apr. 3, 1973

3,725,062

COLOR DIFFUSION PROCESSES UTILIZING HYDROQUINONES WHICH PROVIDE DYE IMAGE MATERIALS UPON OXIDATION IN ALKALINE CONDITIONS

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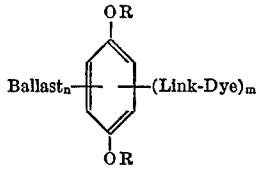
No Drawing. Filed July 6, 1971, Ser. No. 160,062

Int. Cl. G03c 5/54, 1/40, 7/00

U.S. Cl. 96—3 11 Claims

ABSTRACT OF THE DISCLOSURE

Color diffusion transfer processes are described which employ dye image-providing materials which are alkali-cleavable upon oxidation to release a dye or dye precursor which diffuses to a dye image-receiving layer. The compounds have the formula:



wherein Link is S or O, 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 alkali-cleavable upon oxidation.

Color, diffusion transfer processes of the prior art such as U.S. Pat. Nos. 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 characteristics 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 alkali-cleavable upon oxidation.

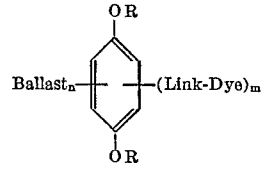
It is therefore an object of this invention to provide a process for producing a photographic transfer image in color in which only the dye portion of the dye image-providing material is transferred to the receiver.

It is another object of this invention to provide processes 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 processes 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 the process of our invention which comprises:

(A) Imagewise exposing 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 alkali-cleavable upon oxidation 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 alkali-cleavable compound nondiffusible during development in an alkaline processing composition;
(3) Dye is a dye or dye precursor;
(4) Link is a S or O linking group;
(5) *n* is an integer of 1 to 3; and
(6) *m* is an integer of 1 to 3;

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

(C) The oxidized developing agent thereby cross-oxidizing each alkali-cleavable compound to cause the compound to cleave at the S or 0 linkage, thus forming an imagewise distribution of diffusible dye or dye precursor as a function of the imagewise exposure of each of the silver halide emulsion layers; and

(D) At least a portion of each of the imagewise distributions of diffusible dye or dye precursor 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 process 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 process 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 process 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 photosensitive elements is disclosed in copending U.S. application Ser. No. 027,991 of Barr, Bush and Thomas filed Apr. 13, 1970 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 process of the present invention can be employed is disclosed in Cole U.S. application Ser. No. 27,990, filed Apr. 13, 1970 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 through 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 formula listed above for the compounds which are alkali-cleavable upon oxidation, 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.

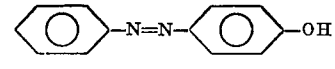
The nature of the ballast group in the formula for the compounds described above (Ballast) is not critical as long as it confers nondiffusibility to the compounds. Typical ballast groups include long-chain alkyl radicals linked directly or indirectly to the compound as well as aromatic radicals of the 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 Link-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.

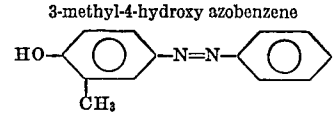
As previously mentioned, Dye in the above formula represents a dye or dye precursor. Such compounds are well known to those skilled in the art and include dyes such as azo, azomethine, indoaniline, indophenol, anthraquinone, triarylmethane, alizarin, etc., and dye precursors such as a leuco dye, a "shifted" 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:

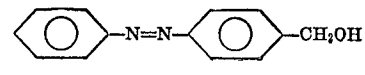
YELLOW DYES

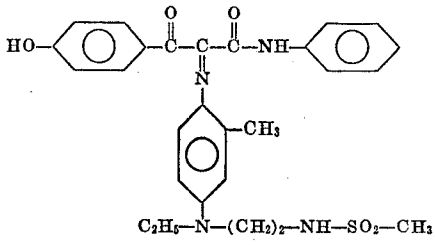
4-hydroxy azobenzene



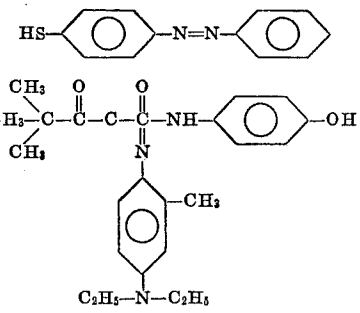
3-methyl-4-hydroxy azobenzene

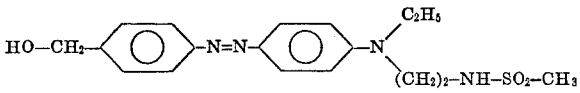




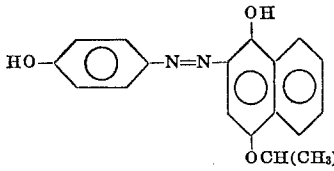


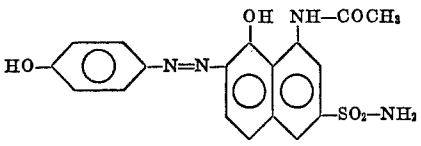
p-Sulfhydryl azobenzene

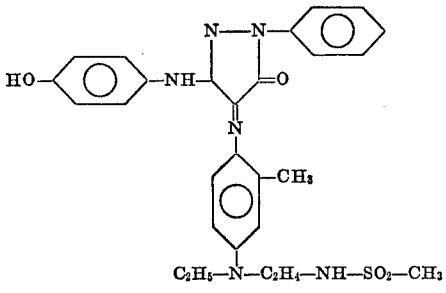




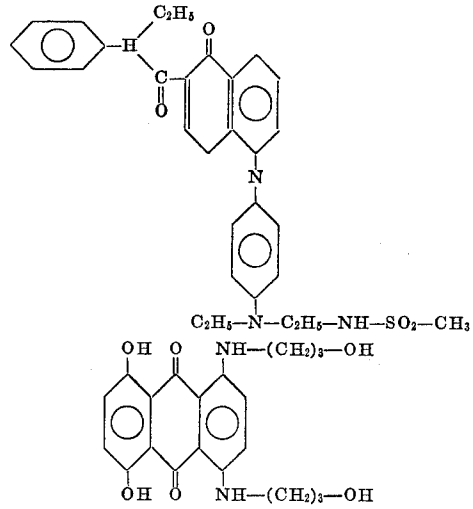
MAGENTA DYES







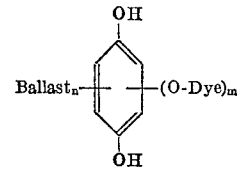
CYAN DYES



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.

After cleavage, the dye or dye precursor moiety is transferred in an alkaline medium to the dye image-receiving layer, either by virtue of its self-diffusivity or by having attached to it one or more solubilizing groups such as —COOH, —SO_3H, —$CONH_2$, —SO_2NO_2, —SO_2NHR, —CONHR, —OH, —NH_2, —SH, etc.

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

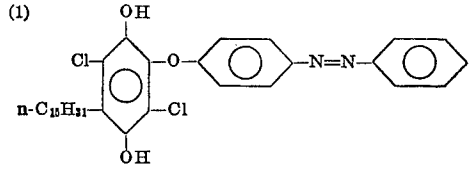


wherein *n* is 1 or 2 and the other substituents have the same definitions defined previously.

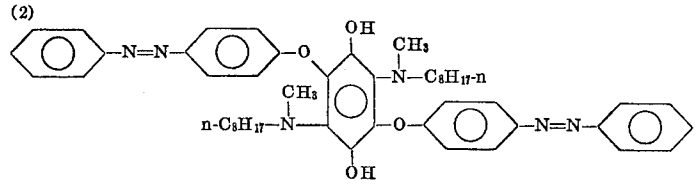
Compounds within this preferred formula include:

Yellow dye-providing hydroquinones

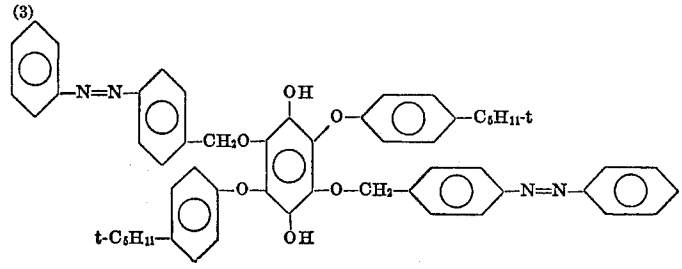
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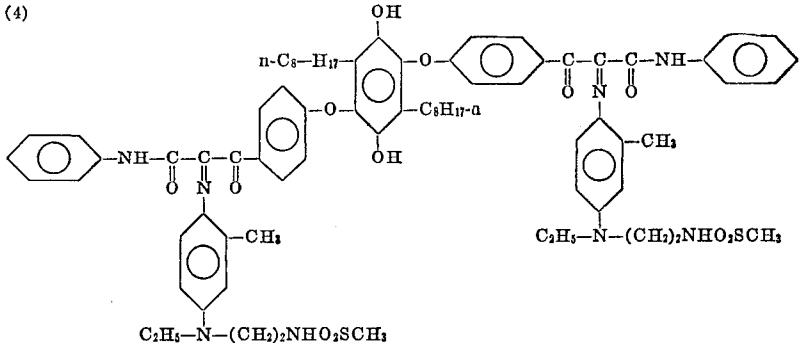
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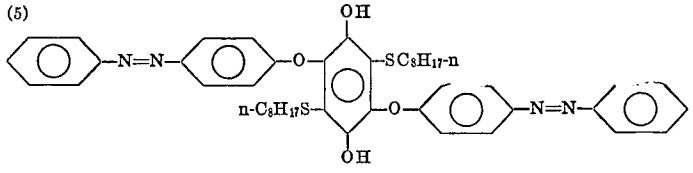
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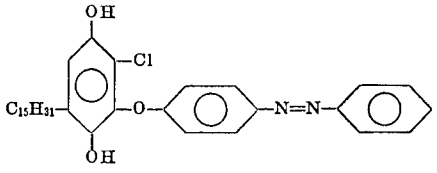
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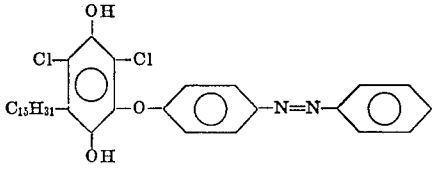
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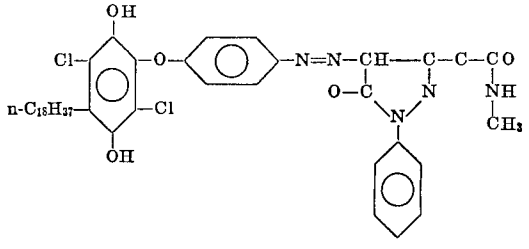
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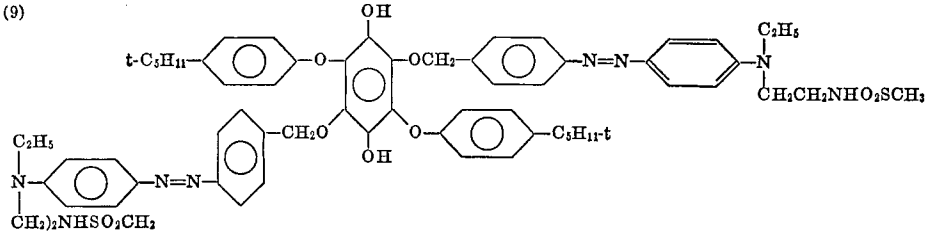
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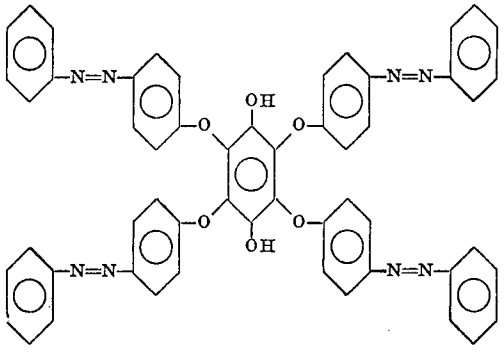
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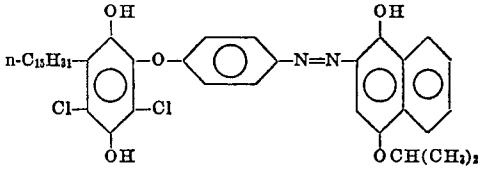


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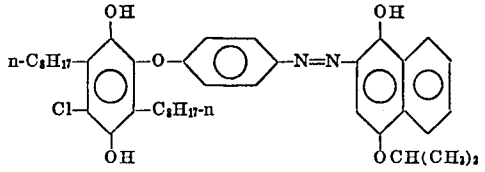


Magenta dye-providing hydroquinones

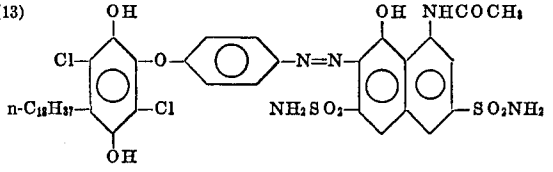
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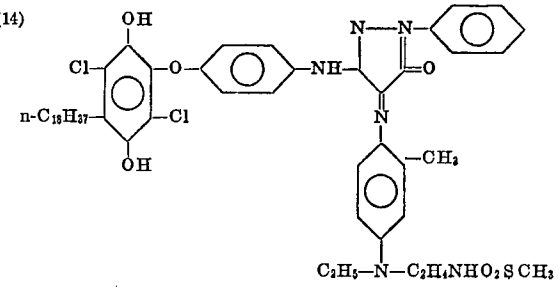
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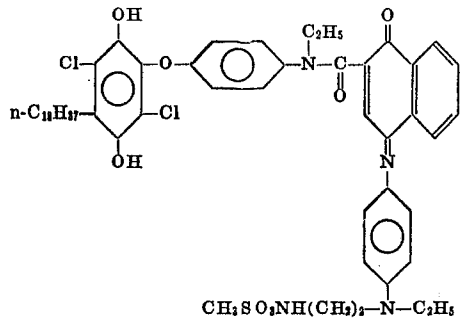


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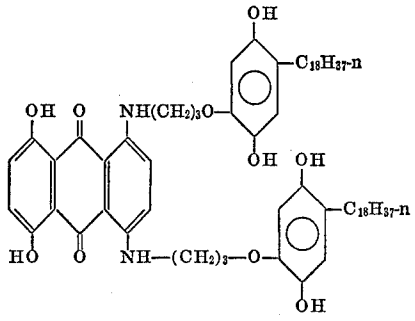


Cyan dye-providing hydroquinones

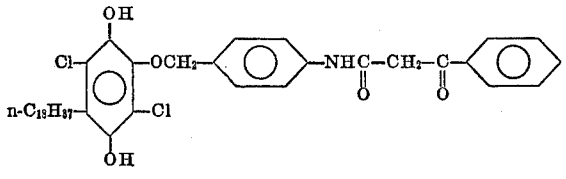
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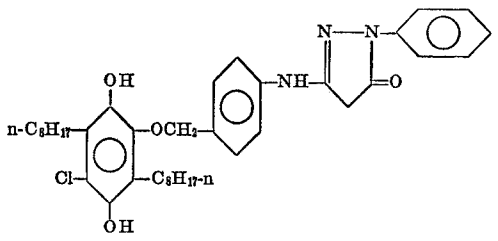
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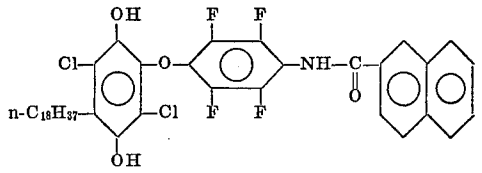
Yellow dye precursor-providing hydroquinone



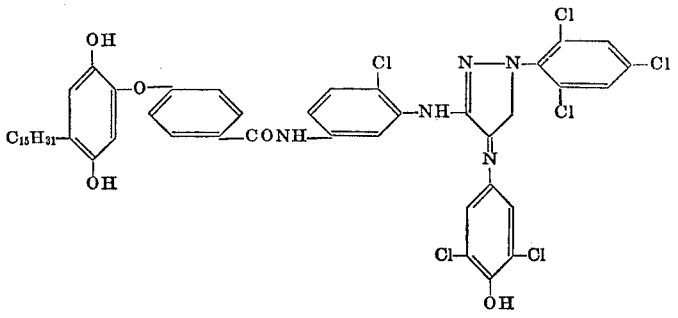
Magenta dye precursor-providing hydroquinone



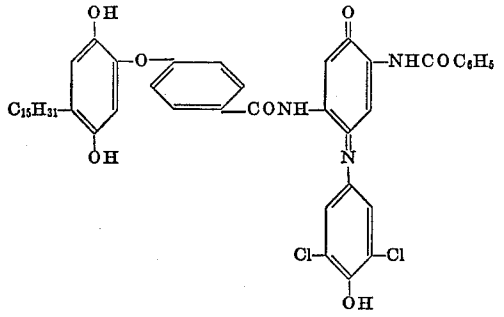
Cyan dye precursor-providing hydroquinone



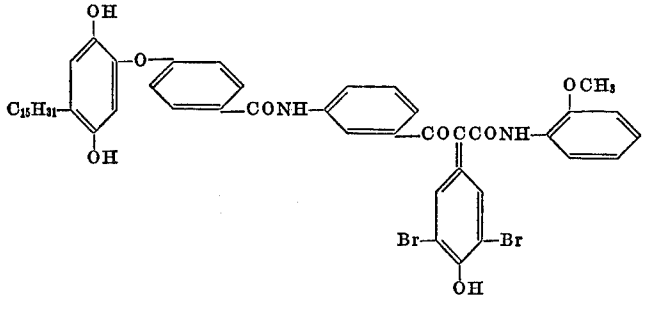
Shifted magenta dye-providing hydroquinone



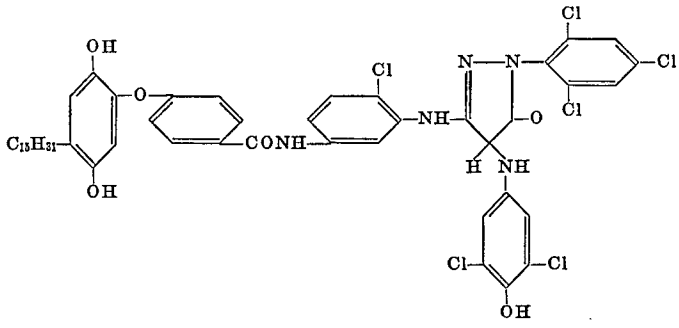
Shifted cyan dye-providing hydroquinone



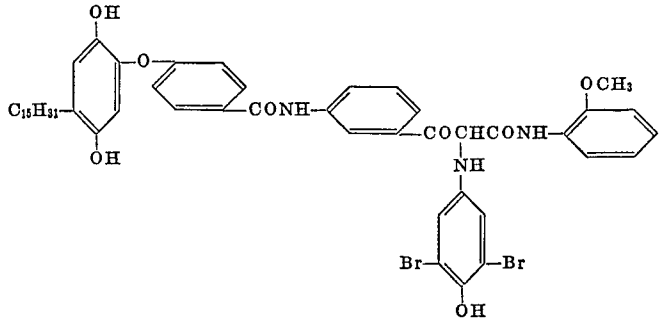
Shifted yellow dye-providing hydroquinone



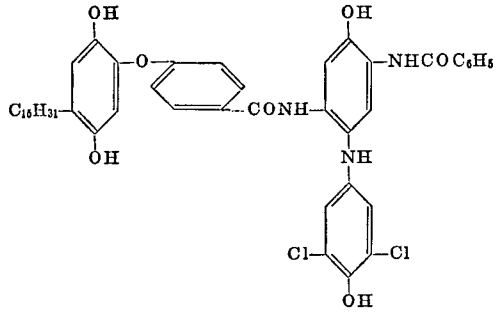
Leuco shifted magenta dye-providing hydroquinone



Leuco shifted yellow dye-providing hydroquinone



Leuco shifted cyan dye-providing hydroquinone



Of the above compounds, especially good results are obtained with

2-chloro-5-n-pentadecyl-3-(p-phenylazophenoxy)-hydroquinone (compound 6);

2,6-dichloro-3-(p-phenylazophenoxy)-5-(n-pentadecyl) hydroquinone (compound 7);

tetra-p-phenylazophenoxy hydroquinone (compound 10); and

3,5-dichloro-2-[p-(1-hydroxy-4-isopropoxy-2-naphthylazo)phenoxy]-6-pentadecylhydroquinone (Compound 11).

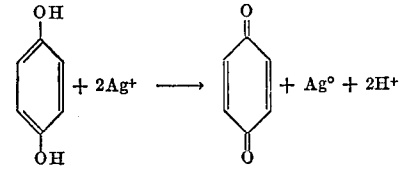
The process of the present invention may be used to produce images in single or multicolors. In a three-color system, each silver halide emulsion layer of the film assembly will have associated therewith a dye image-providing material possessing a spectral absorption range substantially complementary 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 contiguous to the silver halide emulsion layer.

The concentration of the alkali-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, alkali-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.

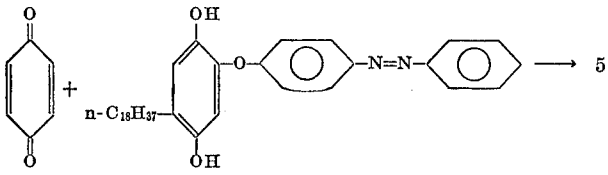
In carrying out the process of our invention, a silver halide developing agent which may be employed in the processing composition or may be incorporated in the photosensitive element to be activated by the alkaline processing composition, is oxidized upon development and reduces silver halide to silver metal. The oxidized developer then cross-oxidizes the alkali-cleavable compound to cause the compound to cleave and form an imagewise distribution of diffusible dye or dye precursor. The alkali-cleavable compound in its oxidized state behaves like a vinylic ester and under the alkaline conditions of the processing composition is hydrolyzed.

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 process of the invention:

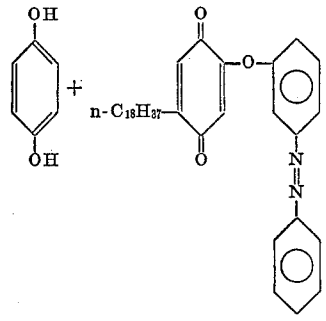
(1) Development of a latent image with hydroquinone, thereby oxidizing it to quinone.



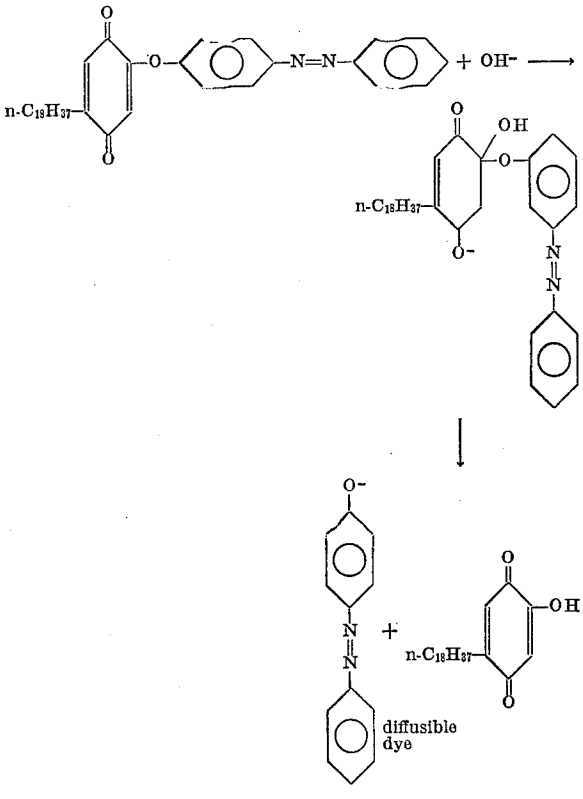
(2) Cross-oxidation step in which quinone is reduced and dye-releasing compound is oxidized.



Ozidized developer — Dye releasing compound



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



diffusible dye

Any silver halide developing agent can be employed in our invention as long as it cross-oxidizes with the alkali-cleavable compounds described herein. Specific examples of suitable developers include

hydroquinone,
N-methyl-aminophenol,
phenidone,
dimezone,
ascorbic acid,
aminophenols,
N-N-diethyl-p-phenylenediamine,
3-methyl-N-N-diethyl-p-phenylenediamine,
3-methoxy-N-ethyl-N-ethoxy-p-phenylenediamine, etc.

In addition, 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.

In using the alkali-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 with the alkali-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 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 May 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, pages 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 is 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, p. 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 alkali-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 porcessing 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 siliver halide emulsion of the multilayer photographic elements employed in the process 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, merocyanine, 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 hetrocyclic 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, thiazolinones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxalkyl, 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. 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 employed in the process 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. Emulsions that contain silver halide grains having substantial surface sensitivity can be used, and emulsions that contain silver halide grains having substantial sensitivity inside the grains can be used such as those described in Davey et al. U.S. Pat. 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; Knott 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. 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 issued May 27, 1952.

The rupturable container employed in the process of 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 employed in the process of 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; 3,121,011; and 3,427,158.

Generally speaking, except where noted otherwise, the silver halide emulsion layers employed in the process of this 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 facilitate 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 trimethyl-ammonium 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 in carrying out the process of the invention will usually increase the stability of the transferred image. Generally, the pH-lowering material will effect a reduction in the pH of the image layer from about 13 or 14 to at least 11 and preferably 5–8 within a short time after imbibition. For example, polymeric acids as disclosed in U.S. Pat. 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 the process of our invention is the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 12, and preferably containing a developing agent as described previously. The solution also preferably contains a viscosity-increasing compound such as a high-molecular-weight polymer, e.g., a water-soluble ether inert to alkaline solutions such as hydroxyethyl cellulose or alkali metal salts of carboxymethyl cellulose such as sodium carboxymethyl cellulose. A concentration of viscosity-increasing compound of about 1 to about 5% by weight of the processing composition is preferred which will impart thereto a viscosity of about 100 cps. to about 200,000 cps. In certain embodiments of our invention, an opacifying agent, e.g., TiO_2, carbon black, etc., may be added to the processing composition.

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

The alkaline solution-permeable, substantially opaque, light-reflective layer employed in certain embodiments of 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 employed in the process of this invention can be any material as long as it does not deleteriously effect the photographic properties of the film unit and is dimensionally stable. Typical flexible sheet materials include cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethyleneterephthalate) film, polycarbonate film, poly-α-olefins such as polyethylene and polypropylene film, and related films or resinous materials as well as glass, 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 19, 1964; and water soluble adducts of glycidol 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 Van Campen 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 15, 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. 28, 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 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 I

A solution of 42.4 g. (0.167 mol) of p-phenylazo phenol, potassium salt, monohydrate, dissolved in 400 ml. of absolute ethanol is cooled to Dry-Ice temperature and stirred vigorously while a solution of 5.00 g. (0.0278 mol) of fluoranil in 100 ml. absolute ethanol is added slowly (½ hour). A dark red precipitate forms immediately upon adding the fluoranil. After the addition, the reaction mixture is stirred slowly and allowed to come to room temperature overnight (18 hours). The red solid is filtered from the reaction mixture, washed with ethanol, then water, and dried partially in the air. The solid is recrystallized from 600 ml. of p-dioxane to give 12.0 g. (48.3%) of tetra-p-phenylazophenoxy - 1,4-benzoquinone, M.P. 250–254° C.

Example II

To a solution of 2.29 g. (0.0124 mol) of hydrazobenzene dissolved in 100 ml. of benzene is added 10.0 g. of tetra-p-phenylazophenoxy-1,4-benzoquinone suspended in 200 ml. of nitrobenzene. The resulting suspension is heated with stirring, on the steam bath. Complete solution occurs in about 10 minutes and the color changes from red to a light yellow. The hot solution is filtered, cooled to room temperature and about 1 liter of cyclohexane is added with stirring. The light yellow precipitate is collected, washed with hot cyclohexane, and dried in air at room temperature to give 8.70 g. (85%) of tetra-p-phenylazophenoxy hydroquinone, M.P. 237.5–239° C. (Compound 10).

Example III

A single layer light-sensitive element is prepared by dissolving .3 g. of Compound 10 in 0.6 ml. of diethyl lauramide, and 3.0 ml. of 2-methyltetrahydrofuran. This solution is dispersed in 15.5 ml. of aqueous gelatin with a colloid mill. One milliliter of tri-isopropyl naphthalene sulfonate as a 5% solution is added to aid in dispersion. To this is added 3 milliliters 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 10.

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-tributylammonium 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 IV

Example III is repeated, but using 0.5 g. of Compound 10 and 0.94 ml. of diethyl lauramide. Similar results are obtained.

Example V

In 500 ml. of chloroform, 31.8 g. (0.1 mole) of n-pentadecyl-1,4-benzoquinone is dissolved. The solution is cooled in an ice bath and with vigorous stirring a stream of dry hydrogen chloride gas is passed through as rapidly as possible without allowing the temperature to exceed 10° C. and as fast as the gas is absorbed. A thick white precipitate is formed. After about one hour the color of the solution is discharged and the reaction appears complete. The solid is collected to give 27 g. of off-white crystals (M.P. 98–101° C.). An additional 4.6 g .of material is obtained from the evaporation of the chloroform and recrystallization from hexane. This is not further characterized other than being identified as the mono-chloro hydroquinone.

The combined product (31.5 g.) is dissolved in a mixture of 150 ml. of acetic acid and 150 ml. of acetone and oxidized by the dropwise addition, with stirring at room temperature, of a solution of 15 g. sodium dichromate dihydrate in 100 ml. of glacial acetic acid. Stirring is continued for one hour, and then the solution is cooled in ice and diluted with an equal volume of water. The solid is collected and washed with water and dried to give 30 g. of a yellow crystalline solid, M.P. 77–80° C. with preliminary softening at 67°. Recrystallization from ethanol gives 26.3 g. of yellow crystals, M.P. 78–80° C. with preliminary softening at 70° C. This is the quinone of the above monochloro hydroquinone.

To 400 ml. of chloroform is added 21.2 g. of this material and the above chlorination is repeated. The resulting material is then oxidized as above to give, after two recrystallizations from ethanol (using 20 ml. of solvent/gram of crude product), 11 g. of light yellow needles (M.P. 65–66° C.) of 2,3-dichloro-5-pentadecyl-1,4-benzoquinone.

A solution of 7.74 g. (0.02 mole) of 2,3-dichloro-5-n-pentadecyl-1,4-benzoquinone in 100 ml. of tetrahydrofuran is cooled in an ice bath to 0° C. To this is added 5.2 g. (0.02 mole) of p-phenlyazo phenol, potassium salt monohydrate, and the solution is stirred at 0° C. for one hour. The mixture is then poured over cracked ice and refrigerated for 24 hours. The sticky brown solid is collected, washed with water and sluried with cold methanol to give 9.4 g. (85.5%) of crude product. Two recrystallizations from ethanol gives 5.9 g. (53.5%) of dark, red brown product.

Two grams of this quinone are reduced with an equivalent of hydrazobenzene in hexane by refluxing on a steam bath for 30 min. The chilled hexane gives 1.6 g. (80%) of crude product (M.P. 84–87° C.) sintering at 70° C. After two recrystallizations from heptane (using 20 ml./g. of solvent/crude product) there is obtained a pure yellow powder (M.P. 86–87.5° C.) sintering at 72° C., becoming marked at 80° C. This compound is identified as 2-chloro-5-n-pentadecyl - 3 - (p-phenylazophenoxy)-hydroquinone (Compound 6).

Example VI

Compound 6 is dispersed as described in Example III and coated on a support with 150 ml./ft.^{2} of a silver bromoiodide emulsion, 80 mg./ft.^{2} of Compound 6 and 120 mg./ft.^{2} of gelatin. A 100 mg./ft.^{2} gel overcoat is also provided.

This element is exposed to a graduated-density multicolor test object and then immersed in a solution containing 0.5 g./l. of methyl-hydroxy methyl Phenidone, 63 g./l. of sodium sulfite, 20 g./l. of sodium hydroxide, and 28 g./l. of hydroxyethyl-cellulose. It is then placed in contact with the receiver sheet of Example III. Upon separation after one minute at about 24° C., a reproduction of the test object in yellow dye is obtained.

Example VII

One gram of 2,3-dichloro-5-n-pentadecylbenzoquinone is dissolved in a mixture of 50 ml. of 2-methoxyethanol and 5 ml. of concentrated hydrochloric acid. Two grams of ferric chloride hexahydrate is added, and the solution is heated on a steam bath for 18 hours. The cooled solution is diluted with water and the crude product (ca. 1.1 g.) is added to a solution of 2 g. of sodium dichromate dihydrate in 20 ml. of concentrated hydrochloric acid, heated for 30 min. on a steam bath, cooled and poured into 100 ml. of cold water. The solid which forms is collected, washed with water, dried, and recrystallized three times from ethanol to give 0.6 g. of 2,3,6-trichloro-5-n-pentadecyl-1,4-benzoquinone, M.P. 76–76.5° C.

A solution of 10 g. (0.0237 mole) of this compound in 50 ml. of p-dioxane is prepared. To this is added dropwise with stirring a solution of 6.03 (0.0237 mole) of p-phenylazophenol potassium salt, monohydrate dissolved in 50 ml. of p-dioxane and 10 ml. of distilled water. The reaction mixture is heated to reflux for 15 min. and then cooled to room temperature and the brown oil is added to an excess of water with stirring. After 30 min., the oil solidifies to give 12.75 g. (92.2%) of the crude product, M.P. 81–84° C. After two recrystallizations from isopropyl alcohol, 9.70 g. (70.2%) of a brick red solid is obtained, M.P. 84.5–86.5° C. This compound is the intermediate 2,6-dichloro - 3 - (p-phenylazophenoxy) - 5 - (n-pentadecyl)-1,4-benzoquinone.

A solution of 5.83 g. (0.010 mole) of this intermediate quinone is prepared with 100 ml. of cyclohexane. The solution is warmed to 60° C. and stirred as a solution of 1.84 g. (0.0100 mole) of hydrazobenzene in 100 ml. of cyclohexane is added slowly. The mixture is heated at reflux for 15 min., cooled to room temperature, and the orange solid which precipitates is recrystallized twice from acetonitrile to give 3.95 g. (67.4%) of 2,6 dichloro-3-(p-phenylazophenoxy) - 5 - (n - pentadecyl)hydroquinone, M.P. 104.5–108.5° C. (Compound 7).

Example VIII

Compound 7 is dispersed 1:2 in the high boiling solvent diethyl lauramide in gelatin. On a support, 150 mg./ft.^{2} of a direct positive AgBrI emulsion is coated in 120 mg./ft.^{2} of gelatin. In a second layer is coated 80 mg./ft.^{2} of Compound 7 dispersed as above in 200 mg./ft.^{2} of gelatin. An overcoat of 80 mg./ft.^{2} of gelatin is provided.

This coating is exposed to a graduated-density multicolor test object and immersed in a developer composition containing 39 g./l. Elon, 0.6 g./l. methyl-hydroxy methyl Phenidone, 32 g./l. hydroxyethyl cellulose, 12 g./l. sodium sulfite, and 20 g./l. of sodium hydroxide. It is then rolled into contact with a receiver sheet containing a coascervate of mordants N1n-hexadecyl-N-morpholinium, ethosulfate and methyl-tri-n-dodecylammonium-p-toulene sulfonate in gelatin. An excellent positive yellow dye reproduction of the test object is obtained on the receiver sheet at the end of one minute.

Example IX

A solution of 1.66 g. (0.005 mole) of 4-isopropoxy-2-[p-hydroxyphenylazo]-1-naphthol in 20 ml. of dry tetrahydrofuran is treated with 15 ml. of methanol containing sodium methoxide (0.28 g., 0.005 ml.) and the solvents are removed under vacuum with gentle warming. The sodium salt of the dye thus obtained (2.03 g.) is dissolved in 25 ml. of dry dimethylformamide and added, at 15–17° C., to a stirred solution of 2.95 g. of 2,3,6-trichloro-5-n pentadecyl-1,4-benzoquinone (Example VII), in 50 ml. of dry dimethyl formamide. Stirring is continued for one hour at 25° C. and then the reaction mixture is allowed to stand for 24 hours at 25° C. whereupon it is poured into ice water.

This magenta dye is taken up in benzene, washed with water, and concentrated to 50 ml.

This solution is refluxed with 1.8 g. (0.01 mole) of hydrazobenzene for 4 hours and then is cromatographed on 200 g. of silica (grade 62, Davison Chemical Co.). Development with 1:1 benzene-hexane gives a forecut of azo benzene. Subsequent development with benzene gives unreduced quinone and magenta dye which is recromatographed on 50 g. of silica to give a forecut of unreduced quinone, and a filtrate fraction containing 1.0 g. (30%) of the desired product, 3,5-dichloro-2-[p-(1-hydroxy-4-isopropoxy-2-naphthylazo)phenoxy] - 6 - pentadecyl-hydroquinone (Compound 11).

Example X

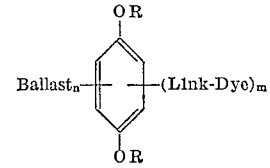
Compound 11 is coated in a manner identical to that described for Compound 7 in Example VIII. It is exposed and processed identically as in Example VIII and gives an excellent magenta dye reproduction of the test object on the receiver sheet.

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. 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 alkali-cleavable upon oxidation 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 alkali-cleavable compound nondiffusible during development in an alkaline processing composition;

(3) Dye is a dye or dye precursor;

(4) Link is an S or O linking group;

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

(6) 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 alkali-cleavable compound to cause said compound to cleave, thus forming an imagewide distribution of diffusible dye or dye precursor 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 diffusing to a dye image-receiving layer to provide said transfer image.

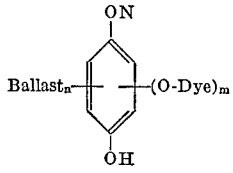
2. The process of claim **1** wherein said treatment step (B) is effected by

(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 processing 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 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.

3. The process of claim **1** wherein said compound which is alkali-cleavable upon oxidation has the formula:



wherein:

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

(2) Dye is a dye or dye precursor;

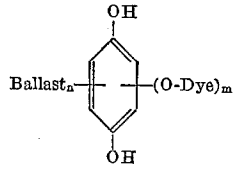
(3) *n* is an integer of 1 to 2; and

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

4. The process of claim **1** wherein said compound is 2-chloro-5-n-pentadecyl - 3 - (p-phenylazophenoxy)hydroquinone; 2,6-dichloro - 3 - (p-phenylazophenoxy)-5-(n-pentadecyl)hydroquinone; tetra-p-phenylazophenoxy hydroquinone; or 3,5 - dichloro-2-[p-(1-hydroxy-4-isopropoxy-2-naphthylazo)phenoxy]-6-pentadecylhydroquinone.

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

(A) image-wise 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-providing material, each said dye image-providing material comprising a compound which is alkali-cleavable upon oxidation having the formula:



wherein:

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

(2) Dye is a dye or dye precursor;

(3) *n* is an integer of 1 to 2; and

(4) *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 alkali-cleavable compound to cause said compound to cleave, thus forming an imagewise distribution of diffusible dye or dye precursor 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 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.

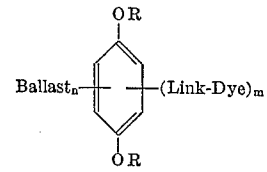
6. A process for producing a photographic transfer image in color comprising:

(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; and

(c) 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 alkali-cleavable upon oxidation 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 alkali-cleavable compound nondiffusible during development in an alkaline processing composition;

(3) Dye is a dye or dye precusor;

(4) Link is an S or 0 linking group;

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

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

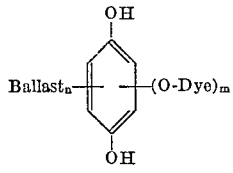
(B) developing each said exposed silver halide emulsion layer with a silver halide developing agent thereby causing said developing agent to become oxidized;

(C) said oxidized developing agent thereby cross-oxidizing each said alkali-cleavable compound to cause said compound to cleave, thus forming an imagewise distribution of diffusible dye or dye pre-

cursor 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 diffusing to said dye image-receiving layer to provide said transfer image viewable through said transparent support.

7. The process of claim **6** wherein said compound which is alkali-cleavable upon oxidation has the formula:



wherein:

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

(2) Dye is a dye or dye precursor;

(3) n is an integer of 1 to 2;

(4) m is an integer of 1 to 3.

8. The process of claim **6** wherein said compound is 2-chloro-5-n-pentadecyl - 3 - (p-phenylazophenoxy)hydroquinone; 2,6 - dichloro-3-(p-phenylazophenoxy)-5-(n-pentadecyl)hydroquinone; tetra-p-phenylazophenoxy hydroquinone; or 4-isopropoxy-2-[p-3,5-dichloro-6-pentadecylhydroquinonyloxy)phenylazo]-1-naphthol.

9. The process of claim **6** wherein said photosensitive element includes:

(a) a transparent sheet superposed over the layer outermost from the transparent support of said photosensitive element; and

(b) a rupturable container containing an alkaline processing composition including an opacifying agent, said rupturable container being positioned transverse a leading edge of said photosensitive element so that a compressive force applied to said container will effect a discharge of the container's contents between said transparent sheet and the outermost layer of said photosensitive element;

said imagewise exposure being effected through said transparent sheet; said photosensitive element, said transparent sheet and said rupturable container comprising a photographic film unit; said film unit containing said developing agent; and applying compressive force to said rupturable container to effect said discharge of said processing composition between said transparent sheet and said outermost layer of said photosensitive element.

10. The process of claim **6** wherein said developing step (B) is effected by:

(a) superposing a substantially opaque process sheet over the layer outermost from the transparent support of said photosensitive element after exposure thereof;

(b) positioning a rupturable container containing an alkaline processing composition between said exposed photosensitive element and said process sheet; and

(c) applying a compressive force to said rupturable container to effect said discharge of said processing composition between said process sheet and said exposed photosensitive element;

said photosensitive element, said process sheet and said rupturable container comprising a photographic film unit, said film unit containing said developing agent.

11. 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;

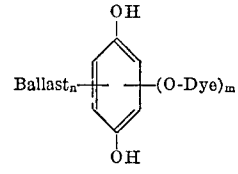
(b) an alkaline solution-permeable, substantially opaque light-reflective layer;

(c) a red-sensitive silver 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;

each said dye image-providing material comprising a compound which is alkali-cleavable upon oxidation having the formula:



wherein:

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

(2) Dye represents a dye or dye precursor;

(3) n is an integer of 1 to 2; and

(4) 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 alkali-cleavable compound to cause said compound to cleave, thus forming an imagewise distribution of diffusible dye or dye precursor 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 diffusing to said dye image-receiving layer to provide said transfer image viewable through said transparent support.

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NORMAN G. TORCHIN, Primary Examiner

A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

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