

1

3,728,113

SELECTIVE TRANSFER SYSTEM AND COMPOUNDS FOR EMPLOYMENT THEREIN

Richard W. Becker, John A. Ford, Jr., Donald L. Fields, and Delbert D. Reynolds, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

No Drawing. Filed July 6, 1971, Ser. No. 160,070

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

U.S. Cl. 96—3

22 Claims

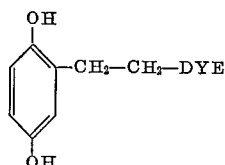
ABSTRACT OF THE DISCLOSURE

A photographic element is provided in which a cleavable compound is employed to effect the imagewise elimination of a selected chemical moiety, such as a dye, a silver halide solvent, an antifoggant, a fixing agent, a toner, a hardener, a silver complexing agent, a fogging agent, a coupler, a sensitizer, a desensitizer, a developer, an oxidizing agent, etc. Color diffusion transfer processes and film units employing such cleavable compounds are also described.

This invention relates to the art of photography. More particularly, this invention relates to the imagewise elimination of chemical entities from compounds which are cleavable upon oxidation in an alkaline medium.

Color diffusion transfer processes of the prior art such as U.S. Pat. No. 2,983,606 generally involve the use of a photographic element comprising a support, at least one silver halide emulsion layer, and containing therein or contiguous thereto a "dye developer." In the exposed areas of the element, the dye developer is oxidized by latent image silver thus becoming immobilized. In the unexposed areas of the element, the dye developer is unaffected and is allowed to transfer by diffusion, to a receiving sheet or layer to form a dye image.

Typical dye developers consist of a hydroquinone or catechol linked by an ethylene group to a dye moiety as follows:



In the exposed areas of the photosensitive elements, the dye developer is oxidized to the quinone and immobilized, while in the unexposed areas the dye developer can diffuse to a receiver sheet. Since the developer portion of the dye developer is transferred with the dye, the resulting prints may suffer from unwanted staining caused by the presence of the developer in the print in the absence of post treatment. Accordingly, it would be highly desirable to provide a transfer system in which only the desired chemical entity, e.g., the dye, is transferred to the receiver.

It is an object of the present invention to provide novel photographic elements and diffusion transfer film units containing a selectively cleavable compound.

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

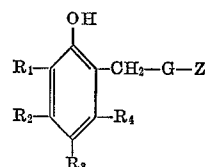
It is still a further object of this invention to provide photographic systems for producing photographic trans-

2

fer 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 photosensitive element according to our invention comprises a support having thereon at least one photosensitive silver halide emulsion layer having associated therewith a compound which is cleavable upon oxidation in an alkaline medium, said compound having the formula



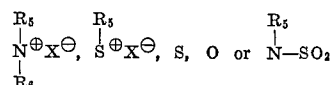
wherein

R₁ represents hydrogen, a hydroxyl group, an amino group, an alkyl group or an aryl group;

R₂ and R₄ each represent hydrogen, an alkyl group or an aryl group;

R₃ represents hydrogen, a hydroxyl group, an alkyl group or an aryl group, with the proviso that when R₁ represents hydrogen, an alkyl group or an aryl group, R₃ must represent a hydroxyl group;

G represents



wherein R₅ and R₆ each represents an alkyl group, an aryl group, or when R₅ and R₆ are taken together with the nitrogen to which they are attached represent a divalent pyridinium group and X[⊖] represents an acid anion;

Z represents a moiety which in combination with G forms a photographically useful compound upon cleavage; and

At least one of R₁, R₂, R₃, R₄ or G—Z being a ballast-ing radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline medium.

When the above-described compounds are oxidized in an alkaline medium, e.g., as a result of cross-oxidation with an oxidized silver halide developing agent, they cleave at the CH₂ linkage. The G—Z moiety is then diffusible in the system. While the compounds described herein have particular application in a diffusion transfer process where it is desired to have a dye entity transferred to a receiving sheet, it has broad application to photographic processes in which it is desired to transfer any organic chemical grouping, after cleavage to a receiver sheet to provide an imagewise differentiation in the chemical and/or physical properties thereof or the organic chemical grouping can remain in the element for a desired result either with or without subsequent treatment. Thus, the organic chemical moiety may be, for example, a silver complexing agent, a silver halide solvent, a fixing agent, a toner, a hardener, an antifoggant, a fogging agent, a coupler, a sensitizer, a desensitizer, a developer, an oxidizing agent or, in the preferred embodiment, a dye or dye precursor. In other words, Z in the above formula may represent any moiety which, in combination with G and in some instances an additional hydrogen atom, forms a photographically useful compound upon cleavage.

3

Specific examples of G-Z include the following:

Antifoggants or development restrainers:

- 1-phenyl-5-mercaptotetrazole
- 6-methyl-4-hydroxytetrazaindene
- 2-mercaptobenzothiazole

Toners:

- 1-phenyl-5-mercaptotetrazole
- 3-mercapto-1,2,4-triazole
- 2,5-dimercapto-1,3,4-thiadiazole

Fixing agents:

- 3-mercaptopropylsulfonic acid
- 1,8-dihydroxy-3,6-dithiaoctane
- 1,9-dihydroxy-3,7-dithianonane
- 1,10-dihydroxy-3,8-dithiadecane, and
- Mercaptomethylacetic acid

Development accelerators:

- N-hydroxydecylpyridinium chloride
- N-hydroxydodecylpyridinium p-toluenesulfonate
- N-hydroxytetradecylpyridinium fluoborate
- N-hydroxydodecyl-N,N,N-trimethylammonium chloride
- N-hydroxydodecyl-N,N,N-trimethylammonium p-toluenesulfonate
- Poly(ethylene oxides) having a molecular weight of at least 460
- Bis[3-(3-hydroxypropylthia)propyl]glutarate
- Bis[2-(2-hydroxyethylthia)ethyl]succinate
- Bis[2-(2-hydroxyethylthia)ethyl]suberate

Developers:

- t-Butylhydroquinone
- Methylhydroquinone
- 2-methyl-5-[2-(4-ethylpiperazino)ethyl]hydroquinone
- 2-methyl-5-[2-(4-methylpiperazino)ethyl]hydroquinone
- 4-hydroxymethyl-4-methyl-2-phenylpyrazolidin-5-one

Hardeners:

- 1,2-bis[2-(dimethylamino)vinylsulfonyl]ethane
- 1,6-bis[2-(diethylamino)vinylsulfonyl]hexane
- 1,3-bis[2-(diethylamino)vinylcarbonyl]propane
- 1,5-bis[2-(diethylamino)vinylcarbonyl]pentane
- Bis(piperidinovinyl) ketone
- Bis(pyrrolidinylvinyl) ketone
- 1,4-bis(pyrrolidinylvinylcarbonyl)butane
- 1,4-bis(piperidinovinylcarbonyl)butane

As previously mentioned, G-Z in the above formula preferably 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, indo-phenol, 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. Patent 2,756,142, etc. Examples of such compounds include the following:

Couplers:

- 3-pyrazolidine-1-phenyl-2-pyrazolin-5-one
- 4-(pivaloylacetamido)pyridine
- 2-(4-pyridylcarbonyl)-1-naphthol
- 2-(2-piperidinoethylcarbonyl)-1-naphthol

Yellow dyes:

- N,N-dimethyl-4-phenylazoaniline
- N,N-diethyl-4-phenylazoaniline
- N,N-diethyl-3-methyl-4-(o-tolylazo)aniline
- N,N-dimethyl-3-methyl-4-(o-tolylazo)aniline
- N,N-dibutyl-3-methyl-4-(o-tolylazo)aniline
- 2-(4-dimethylamino-2-methylphenylimino)-2-phenylcarbamoyletacetophenone
- 2-(4-diethylamino-2-methylphenylimino)-

4

- 2-phenylcarbamoyletacetophenone
- 3',5'-disulfo-2-(4-dimethylamino-2-methylphenylimino)-2-phenylcarbamoyletacetophenone

Magenta dyes:

- 5 2-(4-dimethylaminophenylazo)-4-i-propoxy-1-methoxynaphthalene
- 2-(4-diethylaminophenylazo)-4-i-propoxy-1-butoxynaphthalene
- 10 3-dimethylamino-4-(4-dimethylamino-2-methylphenylimino)-1-phenyl-2-pyrazolin-5-one
- 3-diethylamino-4-(4-dimethylamino-2-methylphenylimino)-1-(p-tolyl)-2-pyrazolin-5-one
- 3-dimethylamino-4-(4-dimethylamino-2-t-butylphenylimino)-1-(p-tolyl)-2-pyrazolin-5-one
- 15 3-diethylamino-4-(4-diethylamino-2-methylphenylimino)-1-phenyl-2-pyrazolin-5-one

Cyan dyes:

- 1,4-bis(dimethylamino)-5-hydroxyanthraquinone
- 1,4-bis(diethylamino)-5-hydroxyanthraquinone
- 20 1,4-dihydro-2-(N,N-diethylcarbamoylet)-4-[4-(N-ethyl-N-hydroxyethylamino)phenylimino]-1-oxonaphthalene
- 1,4-dihydro-2-(N,N-diphenylcarbamoylet)-4-[4-(N-ethyl-N-hydroxyethylamino)phenylimino]-1-oxonaphthalene
- 25 1,4-dihydro-2-(N,N-dimethylcarbamoylet)-4-(4-diethylaminophenylimino)-1-oxonaphthalene
- 1,4-dihydro-2-(N,N-diethylcarbamoylet)-4-(4-diethylaminophenylimino)-1-oxonaphthalene
- 30 1,4-dihydro-2-(N,N-dimethylcarbamoylet)-4-[4-(N-ethyl-N-hydroxyethylamino)-2-methylphenylimino]-1-oxonaphthalene
- 1,4-dihydro-2-(N,N-diethylcarbamoylet)-4-(4-diethylamino-2-methylphenylimino)-1-oxonaphthalene
- 35 1,4-dihydro-2-(N,N-dimethylcarbamoylet)-4-[4-(N-ethyl-N-methylsulfamoyl)phenylimino]-1-oxonaphthalene
- 1,4-dihydro-2-(N,N-diethylcarbamoylet)-4-(4-diethylamino-2-methoxyphenylimino)-1-oxonaphthalene
- 40 1,4-dihydro-2-(N,N-dimethylcarbamoylet)-4-[4-(N-ethyl-N-methylsulfamoyl)phenylimino]-1-oxonaphthalene
- 1,4-dihydro-2-(N,N-diethylcarbamoylet)-4-[4-(N-ethyl-N-methylsulfamoyl)phenylimino]-1-oxonaphthalene
- 45 2-(N,N-diethylcarbamoylet)-4-[4-(N,N-diethylamino)-2-methoxyphenylimino]-1,4,5,6,7,8-hexahydro-1-oxonaphthalene
- 2-(N,N-dimethylcarbamoylet)-4-[4-(N-ethyl-N-methylsulfamoyl)phenylimino]-1,4,5,6,7,8-hexahydro-1-oxonaphthalene

Miscellaneous dyes:

- 9-(2-pyridyl)anthracene
- 3-cyano-5-[4-(N-dimethylaminoethyl-N-ethylamino)-2-methylphenylmethylene]-4-phenyl-2(5H)furanone
- 55 2-(4-dimethylaminophenylazo)pyridine
- 1-(3-dimethylaminopropylamino)-4-methylaminoanthraquinone
- 60 1-[2,5-dimethyl-1-(3-pyridyl)-3-pyrrylmethylene]-3-indenecarboxylic acid
- 2,3-dihydro-6-(3-dimethylaminopropylamino)-1-ethoxycarbonyl-3-methyl-2-oxo-azabenzanthrone
- 1-(2-pyridylazo)-2-naphthol
- 65 p-(phenylazo)benzenesulfonyl chloride
- p-isocyanatophenylazobenzene, etc.

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.

As was previously mentioned, R₁, R₂, R₃, R₄, R₅ and R₆ may each represent, inter alia, an alkyl group or an aryl group. The terms "alkyl" and "aryl" as employed

5

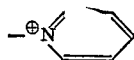
herein include substituted alkyl and aryl groups. Thus, R_1 , R_2 , R_3 , R_4 , R_5 and R_6 may each represent, for example, methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc.; or a substituted alkyl group such as an hydroxyalkyl group, e.g., β -hydroxyethyl, ω -hydroxybutyl, etc., a carboxyalkyl group, e.g., β -carboxyethyl, ω -carboxybutyl, etc., a sulfoalkyl group, e.g., β -sulfoethyl, ω -sulfobutyl, etc., an acyloxyalkyl group, e.g., β -acetoxyethyl, γ -acetoxypropyl, ω -butyryloxybutyl, etc., an alkoxyalkyl group, e.g., β -methoxycarbonyl, ω -ethoxycarbonyl, etc.; or an aralkyl group, e.g., benzyl, phenethyl, etc.; or an aryl group or substituted aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.

Precursors of compounds according to the above-mentioned formula can also be employed in our invention, e.g., replacing an OH in the formula with an acyloxy group which is converted to OH upon alkaline activation, etc.

In a preferred embodiment of the above formula, R_1 is hydrogen, R_2 is an alkyl group preferably containing 8-20 carbon atoms so as to serve as a ballasting radical, R_3 is an hydroxyl group, R_4 is hydrogen, G represents:

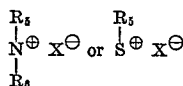


wherein R_5 and R_6 each represents a methyl group or, when taken together with the nitrogen to which they are attached, represent a divalent heterocyclic pyridinium moiety:



and X^- represents an acidic anion.

As was mentioned above, Z is preferably a dye or a dye-forming organic chemical grouping. Upon cleavage, Z taken together with G becomes the dye Z-G-H with the proviso that the dye Z-G is formed when -G- is:



the X^- being liberated.

X^- represents an acid anion, e.g., chloride, bromide, iodide, thiocyanate, sulfamate, perchlorate, p-toluenesulfonate, methylsulfate, ethylsulfate, etc.

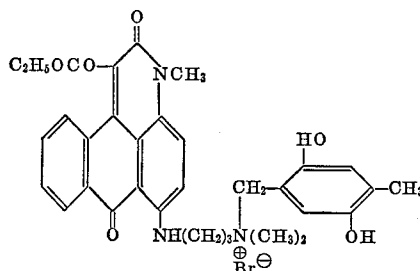
The nature of the group which serves as a ballasting radical in the formula for the compounds described above is not critical as long as it confers nondiffusibility to the compounds. Typical ballast groups include long-chain alkyl radicals linked directly or indirectly to the compound, as well as aromatic radicals of the benzene and naphthalene series, etc. Useful ballast groups generally have at least 8 carbon atoms and may even comprise G-Z, which in a preferred embodiment is a dye or dye precursor.

6

Suitable cleavable dye image-providing materials within the scope of the above-mentioned formula include, for example:

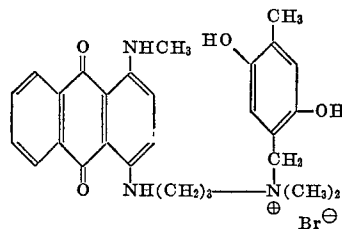
Compound I: (magenta dye-releasing)

N-3-(2,3-dihydro-1-ethoxycarbonyl-3-methyl-2-oxo-3-azabenzanthron-6-ylamino)propyl-N-2,5-dihydroxy-4-methylbenzyl-N,N-dimethylammonium bromide



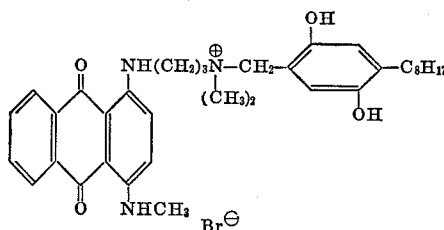
Compound II: (cyan dye-releasing)

N-(2,5-dihydroxy-4-methylbenzyl)-N,N-dimethyl-N-[3-(4-methylamino-1-anthraquinonylamino)propyl]ammonium bromide



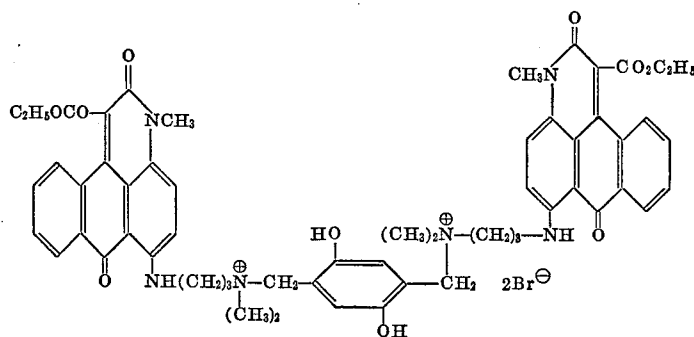
Compound III: (cyan dye-releasing)

N-2,5-dihydroxy-4-octylbenzyl-N,N-dimethyl-N-[3-(4-methylamino-1-anthraquinonylamino)propyl]ammonium bromide



Compound IV: (magenta dye-releasing)

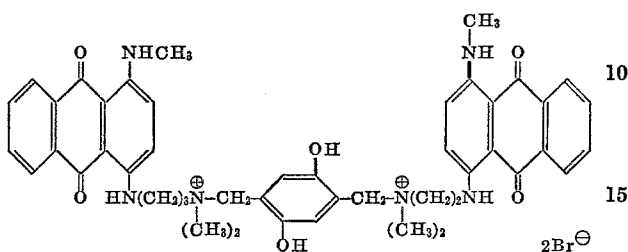
2,5-dihydroxy- α,α' -p-xylylene-bis[N-3-(2,3-dihydro-1-ethoxycarbonyl-3-methyl-2-oxo-3-azabenzanthron-6-ylamino)propyl-N,N-dimethylammonium bromide]



7

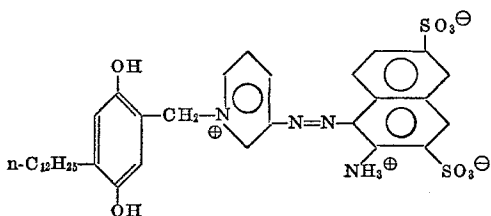
Compound V: (cyan dye-releasing)

2,5-dihydroxy- α,α -p-xylylenebis-[N,N - dimethyl-N-3-(4-methylamino - 1 - anthraquinonylamino)propyl]ammonium bromide}



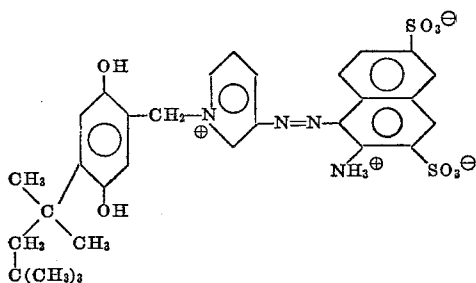
Compound VI: (yellow dye-releasing)

Anhydro-3-(2-amino-3,6-disulfo-1-naphthylazo) - 1-(4-n-dodecyl - 2,5 - dihydroxybenzyl)pyridinium hydroxide (inner salt)



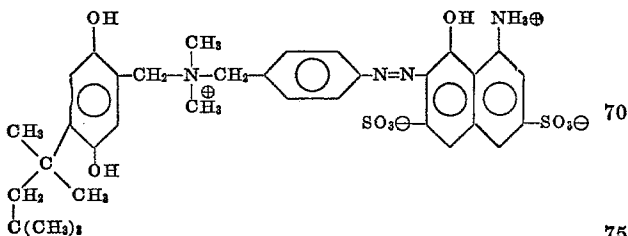
Compound VII: (yellow dye-releasing)

Anhydro-3 - (2-amino-3,6-disulfo-1-naphthylazo)-1-(4-t-octyl-2,5-dihydroxybenzyl)pyridinium hydroxide (inner salt)



Compound VIII

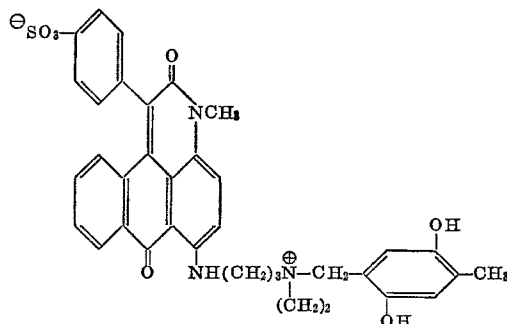
Anhydro-N-[4 - (8-amino-1-hydroxy - 3,6-disulfo-2-naphthylazo)-benzyl] - N - (4-t-octyl-2,5-dihydroxybenzyl) dimethylammonium hydroxide (inner salt)



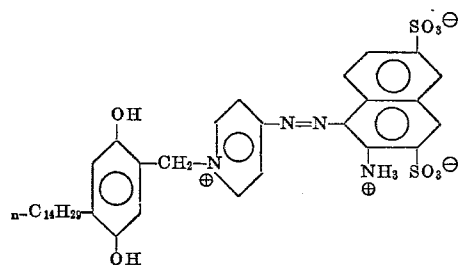
8

Compound IX

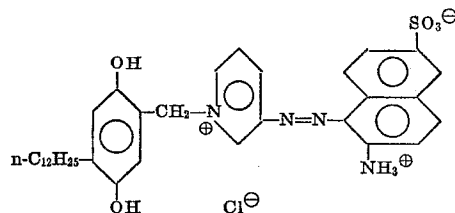
Anhydro - [3-(2,3-dihydro-3-methyl-2-oxo-1-sulfophenyl-3-azabenzanthron - 6 - ylamino)propyl]-N-(2,5-dihydroxy-4-methylbenzyl) - N,N - dimethylammonium hydroxide (inner salt)



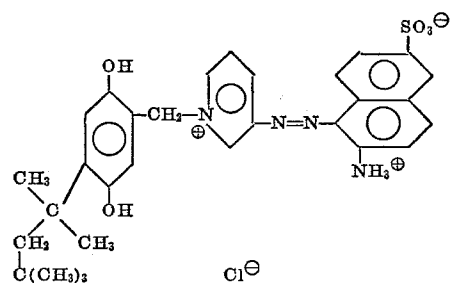
Compound X: (yellow dye-releasing)



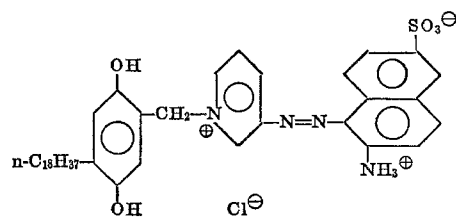
Compound XI: (yellow dye-releasing)



Compound XII: (yellow dye-releasing)

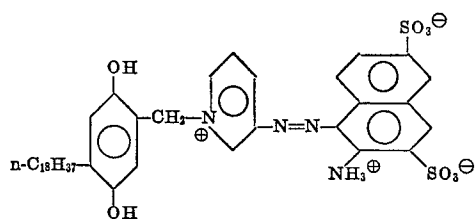


Compound XIII: (yellow dye-releasing)

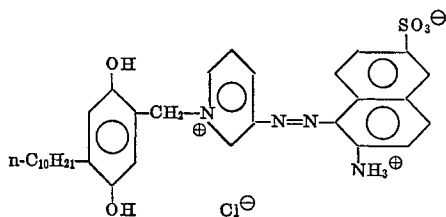


9

Compound XIV: (yellow dye-releasing)

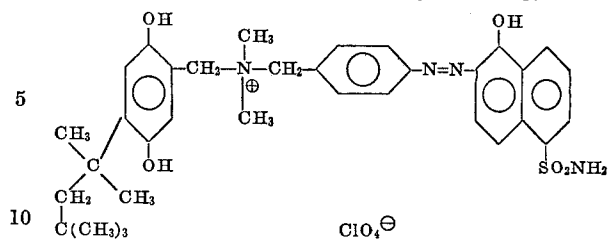


Compound XV: (yellow dye-releasing)



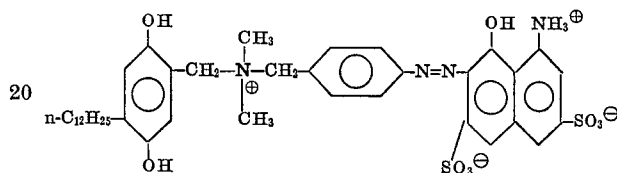
10

Compound XVIII: (yellow dye-releasing)

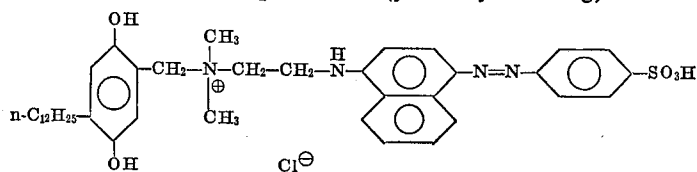


Compound XIX

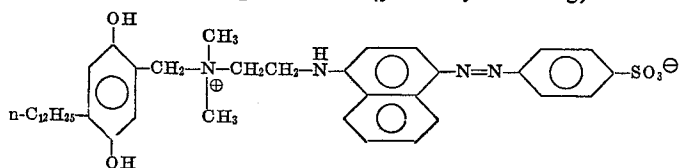
Anhydro-N-[4 - (8 - amino - 1 - hydroxy - 3,6 - disulfo-2-naphthylazo)-benzyl]-N-(4-n-dodecyl - 2,5 - dihydroxy-benzyl)dimethylammonium hydroxide (inner salt)



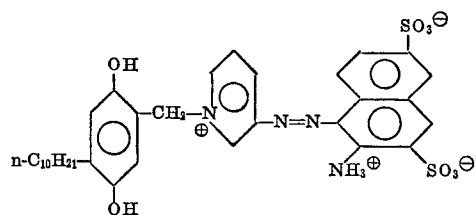
Compound XX: (yellow dye-releasing)



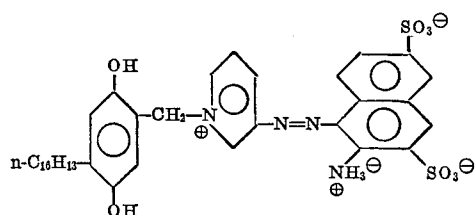
Compound XXI: (yellow dye-releasing)



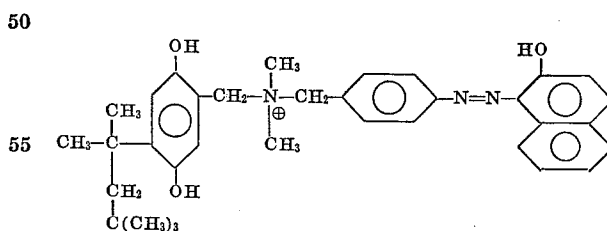
Compound XVI: (yellow dye-releasing)



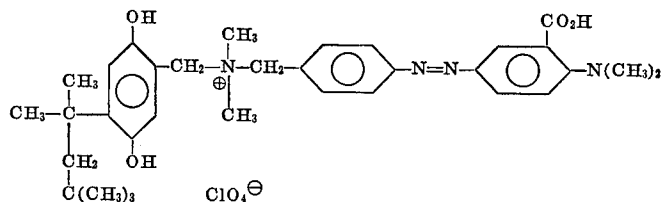
Compound XVII: (yellow dye-releasing)



Compound XXII: (yellow dye-releasing)

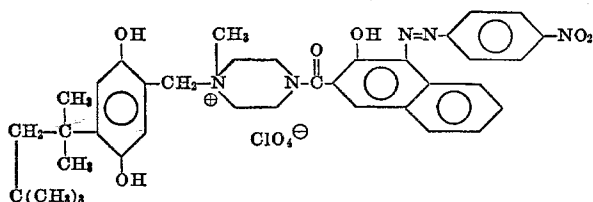


Compound XXIII: (yellow dye-releasing)

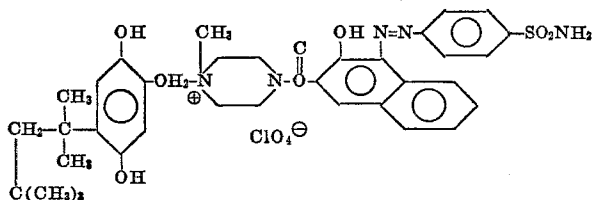


11

Compound XXIV: (yellow dye-releasing)



Compound XXV: (yellow dye-releasing)



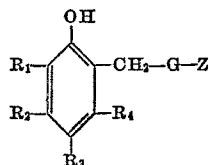
Compound XXVI: (magenta dye-releasing)

N-[3 - (2,3 - dihydro - 3 - methyl-2-oxo-1-sulphophenyl-3-azabenzanthron-6-ylamino)propyl]-N-(2,5-dihydroxy-4-laurylbenzyl)-N,N-dimethylammonium (inner salt)

Another aspect of this invention relates to a photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

- 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;
- a dye image-receiving layer; and
- a rupturable container containing an alkaline processing composition;

the rupturable container being adapted to be positioned during processing of the film unit so that a compressive force applied to the container by the pressure-applying members will effect a discharge of the container's contents within the film unit, said film unit containing a silver halide developing agent, and the dye image-providing material being a compound which is cleavable upon oxidation in an alkaline medium and having the formula:



wherein R_1 , R_2 , R_3 , R_4 and G are defined in the manner previously stated and Z in combination with G represents a dye or dye precursor.

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

- 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;
- the oxidized developing agent thereby cross-oxidizing each cleavable compound to cause the compound to cleave at the methylene 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
- at least a portion of each of the imagewise distribu-

12

tions of diffusible dye or dye precursor diffusing to a dye image-receiving layer to provide a positive 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. Patent 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 positive, 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 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.

13

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 positive, 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.

The film unit or assembly of the present invention may be used to produce positive images in single or multi-colors. 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 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% 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 premeated 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 activated by the alkaline processing composition. Specific examples of developers which can be employed in our invention include:

hydroquinone
N-methylaminophenol
Phenidone
Dimezone
4'-methylphenylhydroquinone
4-methyl-4-hydroxymethyl-3-pyrazolidone
piperidinohexosylreductone
1,2,3,4-tetrahydro-1,4-methanonaphthalene-5,8-diol
N-(2,5-dihydroxy-4-methyl) benzyl-N-methyl-
morpholinium perchlorate
ascorbic acid
aminophenols
N,N-diethyl-p-phenylenediamine
3-methyl-N,N-diethyl-p-phenylenediamine
3-methoxy-N-ethyl-N-ethoxyphenylenediamine, etc.

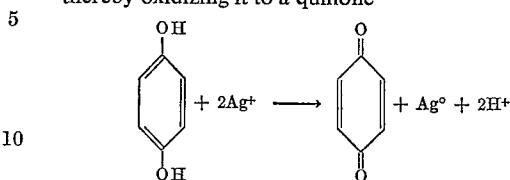
The presence of sulfite ions in the developing composition, e.g., by adding sodium sulfite, has also been found effective in improving dye image discrimination.

In a preferred embodiment of our invention 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 methylene linkage, thus forming an imagewise distribution of diffusible dye or dye precursor which then diffuses to the receiving layer to provide the positive dye image. Although it is not intended to limit the present invention to any particular theory or reaction mechanism, it is be-

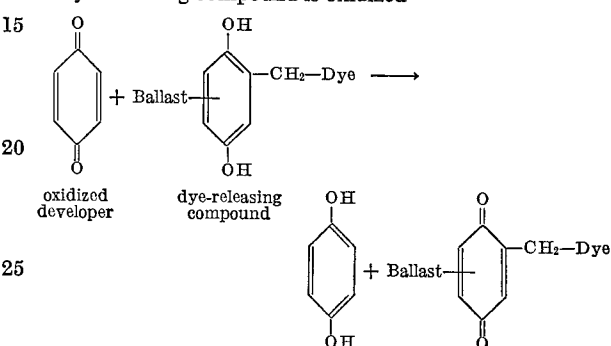
14

believed that the following chemical reactions take place according to a particular process of the invention:

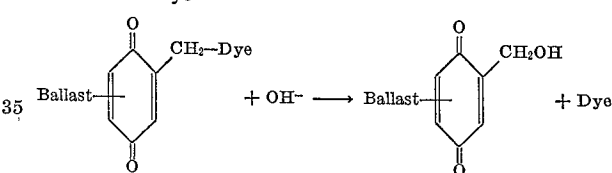
- (1) Development of a latent image with hydroquinone, thereby oxidizing it to a quinone



- (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



The preferred compounds to be employed in the present invention can be prepared in any suitable manner. For example a cleavable compound according to our invention containing an anthraquinone or dihydroazabenzanthrone dye moiety can be prepared by procedures well-known in the art. Typically, a 4-(dialkylaminoalkylamino)anthraquinone or a 6 - dialkylaminoalkylamino-2,3-dihydro-2-oxo-3-azabenzanthrone and a 2,5-diacetoxy-p-methylbenzyl halide are refluxed in a suitable solvent such as acetonitrile. The reaction mixture is cooled to ambient temperature and the desired diacetoxy derivative of the dye is collected and dried. Deacetylation is typically accomplished by agitating a mixture of the diacetoxy derivative and ethyl alcohol that has been saturated with anhydrous hydrogen chloride at ambient temperature for an extended period, e.g., 72 hours. The deacetylated hydroquinone dye thus obtained is collected and dried. The reaction of 2 molecules of a 4-(dialkylaminoalkylamino)anthraquinone or a 6-dialkylaminoalkyl-2,3-dihydro-2-oxo-3-azabenzanthrone with a 2,5-diacetoxy-p-xylylene halide under the above-described conditions affords the diacetylated derivatives of the corresponding bis(anthraquinone) and bis(2,3-dihydro-2-oxo-3-azabenzanthrone) dyes. Deacetylation is conveniently carried out by the procedure previously given.

A cleavable compound according to our invention containing an azo dye moiety can also be prepared by techniques known in the art. For example, an azo dye can be prepared by coupling a diazotized 3-aminopyridine or a p-dimethylaminomethylaniline with a naphthalene mono- or poly-sulfonic acid. The resulting azo dye is quaternized by reaction with a 2,5-diacetoxybenzyl halide having an alkyl group of from 6 to 20 carbon atoms in the 4-position. The intermediate quaternized diacetoxyhydroquinone dye is deacetylated by the procedure described hereinabove to afford the desired immobile, cleavable compound according to the invention. Diacetoxybenzyl halides em-

ployed in preparing the immobile, cleavable compounds of this invention are conveniently made by the process of D. L. Fields et al., *Journ. Org. Chem.*, 29, 2640 (1964).

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 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 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., U.S. Patent 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:		
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 Patent 443,245, Feb. 25, 1936, who subjected emulsion to Roentgen rays "until an emulsion layer formed therefrom, when developed without preliminary exposure, is blackened up to the apex of its graduation curve"; Szaz British Patent 462,730, Mar. 15, 1937, the use of either light or chemicals such as silver nitrate, organic sulfur compounds and dyes to convert ordinary silver halide emulsions to solarizing direct-positive emulsions; and Arens U.S. Patent 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. Patent 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. Patent 3,367,778; Illingsworth U.S. Patents 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. Patents 2,588,982 issued Mar. 11, 1952 and 2,563,785 issued Aug. 7, 1951; the hydrazides and hydrazones disclosed in Whitmore U.S. Patent 3,227,552 issued Jan. 4, 1966; hydrazone quaternary salts described in Lincoln and Heseltine application Ser. No. 828,064 filed Apr. 28, 1969; or mixture 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. Patents 3,227,550; 3,227,551; 3,227,552; and in British Patent 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. Patent 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 Patent 904,364, p. 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 Patent 1,154,781 issued June 11, 1969. For optimum results, the dye can either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al., U.S. Patent 2,526,632, issued Oct. 24, 1950; Sprague U.S. Patent 2,503,776, issued Apr. 11, 1950; Brooker et al. U.S. Patent 2,493,748, issued Jan. 10, 1950; and Taber et al., U.S. Patent 3,384,486 issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri- or tetranuclear) merocyanines, complex (tri- or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g. enamine hemicyanines), oxonols and hemioxonols. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or lakoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain. The merocyanine dyes can contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoin, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition, supersensitizing addenda which do not absorb visible light can be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S. Patent 2,933,390 issued Apr. 19, 1960 and Jones et al. U.S. Patent 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 bromiodide, silver chlorobromiodide 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. Patent 2,222,264 issued Nov. 19, 1940; Illingsworth U.S. Patent 3,320,069 issued May 16, 1967; and McBride U.S. Patent 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. Patent 2,592,250 issued May 8, 1952; Porter et al. U.S. Patent 3,206,313 issued Sept. 14, 1965; Berriman U.S. Patent 3,367,778 issued Feb. 6, 1968; and Bacon et al. U.S. Patent 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. Patent 2,184,013 issued Dec. 19, 1939; Kendall et al. U.S. Patent 2,541,472 issued Feb. 13, 1951; Berriman U.S. Patent 3,367,778 issued Feb. 6, 1968; Schouwenaars British Patent 723,019 issued Feb. 2, 1955; Illingsworth et al. French Patent 1,520,821 issued Mar. 4, 1968; Illingsworth U.S. Patent 3,501,307 issued Mar. 17, 1970; Ives U.S. Patent 2,563,785 issued Aug. 7, 1951; Knott et al. U.S. Patent 2,456,953 issued Dec. 21, 1948; and Land U.S. Patent 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. Patent 1,623,499 issued Apr. 5, 1927; Waller et al. U.S. Patent 2,399,083 issued Apr. 23, 1946; McVeigh U.S. Patent 3,297,447 issued Jan. 10, 1967; and Dunn U.S. Patent 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. Patent 2,886,437 issued May 12, 1959; Dann et al. U.S. Patent 3,046,134 issued July 24, 1962; Carroll et al. U.S. Patent 2,944,900 issued July 12, 1960; and Goffe U.S. Patent 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. Patent 2,131,038 issued Sept. 27, 1938; and Allen et al. U.S. Patent 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper U.S. Patent 2,886,437 issued May 12, 1959; and Heimbach et al. U.S. Patent 2,444,605 issued July 6, 1948; the mercury salts as described in Allen et al. U.S. Patent 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al. U.S. Patent 3,287,135 issued Nov. 22, 1966; the sulfocatechols described in Kennard et al. U.S. Patent 3,236,652 issued Feb. 22, 1966; the oximes described in Carroll et al. British Patent 623,448 issued May 18, 1949; nitron nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Patent 2,403,927 issued July 16, 1946; Kennard et al. U.S. Patent 3,266,897 issued Aug. 16, 1966; and Luckey et al. U.S. Patent 3,397,987 issued Aug. 20, 1968; the polyvalent metal salts described in Jones U.S. Patent 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al. U.S. Patent 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al. U.S. Patent 2,566,263 issued Aug. 28, 1951; and Yutzy et al. U.S. Patent 2,597,915 issued May 27, 1952.

The rupturable container employed in this invention can be of the type disclosed in U.S. Patent 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-imperious 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. Patent No. 3,384,483, polymeric materials such as polyvinylamides as disclosed in U.S. Patent 3,421,892, or any of those disclosed in French Patent 2,028,236 or U.S. Patent Nos. 2,992,104; 3,043,692; 3,044,873; 3,061,428; 3,069,263; 3,069,264; 3,121,011; and 3,427,158.

Generally speaking, except where noted otherwise, the silver halide emulsion layers in the invention comprise photosensitive silver halide dispersed in gelatin and are about 0.6 to 6 microns in thickness; the dye image-providing materials are dispersed in an aqueous alkaline solution-permeable polymeric binder, such as gelatin, as a separate layer about 1 to 7 microns in thickness; and the alkaline solution-permeable polymeric interlayers, e.g., gelatin, are about 1 to 5 microns in thickness. Of course these thicknesses are approximate only and can be modified according to the product desired. In addition to gelatin, other suitable hydrophilic materials 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 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 ultra-violet 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 inhibition. 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 alkali 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., TiO₂, 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 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 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.

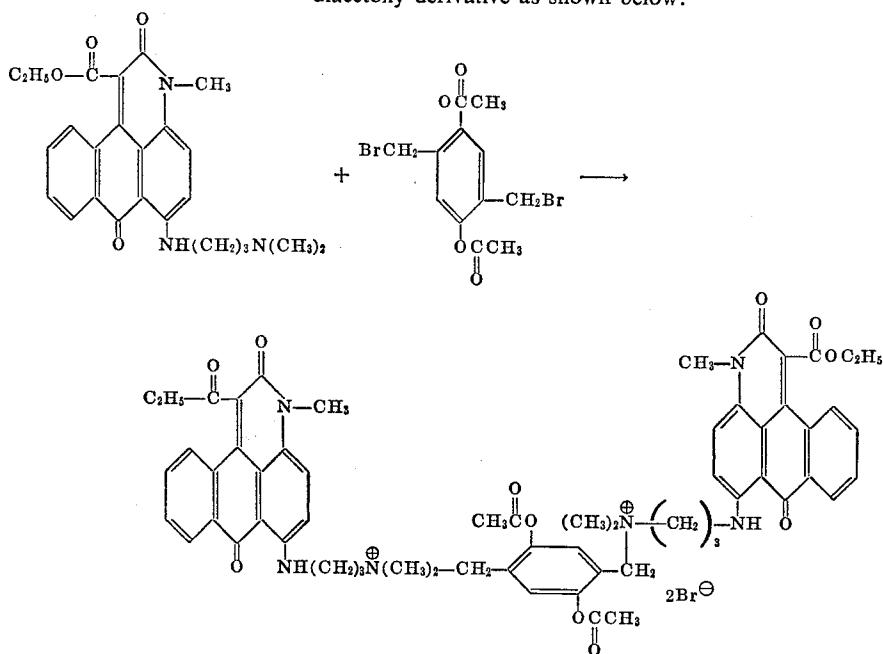
The photographic layers used in the practice of this invention may be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin U.S. Pat. 2,681,294 issued June 15, 1954. If desired, two or more layers 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 1

Compound IV is prepared by deacetylation of its diacetoxy derivative as shown below:



23

A mixture of 15.0 g. (0.0346 mole) of 2,3-dihydro-1-ethoxycarbonyl - 6-(3 - dimethylaminopropylamino)-3-methyl-2-oxo-3-azabenzanthrone, 6.6 g. (0.017 mole) of 2,5-diacetoxy- α,α' -dibromoxylene and 150 ml. of acetonitrile is refluxed for 15 hours with stirring. The reaction mixture is then cooled to room temperature, the crystals are collected on a filter, washed with acetonitrile and dried. A yield of 22.2 g. of red powder melting at 224–226° C. is obtained which is 2,5-diacetoxy- α,α' -p-xylene-bis[N-3-(2,3-dihydro - 1-ethoxycarbonyl-3-methyl-2-oxo-3-azabenzanthron - 6 - ylamino)propyl-N,N-dimethylammonium bromide].

A suspension of 22.2 g. (0.0178 mole) of the diacetoxy derivative described above in 250 ml. of ethyl alcohol is saturated with anhydrous hydrogen chloride. After saturation, the mixture is stirred for 72 hours at ambient temperature. The resulting solid is collected on a filter and dried. A yield of 18.2 g. of magenta crystals of Compound IV melting at 223–226° C. is obtained.

EXAMPLE 2

A single-layer, light-sensitive element is prepared by coating the following layer on a polyethylene terephthalate film support:

gelatin (340 mg./ft.²), negative gelatin-silver bromiodide emulsion (160 mg. gelatin/ft.² and 216 mg. silver/ft.²) and

Compound IX (0.1 millimole/ft.²).

A multilayer image receiving element is prepared by coating the following layers in the order recited on a polyethylene-coated paper support:

- (1) gelatin (745 mg./ft.²), N-ethyl-N-n-hexadecylmorpholinium ethosulfate (150 mg./ft.²) and methyl-tri-n-dodecylammonium p-toluenesulfonate (22.5 mg./ft.²);
- (2) gelatin overcoat (100 mg./ft.²).

A sample of the photosensitive element is exposed to a graduated-density multicolor test object. The exposed photosensitive element is presoaked for 15 seconds in Eastman Kodak Developer DK-50 and then laminated to the image-receiving element which has also been presoaked for 15 seconds in the same developer. After 60 seconds at 25° C., the negative element is stripped away from the image-receiving element to reveal a well-defined negative dye image on the image-receiving element. A spectrophotometric analysis of the transferred dye shows that the image dye consists mainly of 2,3 - dihydro - 6 - (3 - dimethylaminopropylamino) - 3 - methyl - 2 - oxo-1-sulfophenyl-3-azabenzanthrone which is the dye fragment present in Compound IV.

EXAMPLE 3

A multilayer photosensitive element is prepared by coating the following layers in the order recited on a polyethylene terephthalate film support:

- (1) gelatin (500 mg./ft.²) and Compound IX (0.1 millimole/ft.²),
- (2) gelatin interlayer (100 mg./ft.²) and
- (3) negative, gelatin-silver bromiodide emulsion (150 mg. gelatin/ft.² and 216 mg. silver/ft.²).

The photosensitive element is exposed and processed as in Example 2 to obtain a negative dye image on the image-receiving element.

EXAMPLE 4

A multilayer, multicolor, photosensitive element is prepared by coating the following layers in the order recited on a polyethylene terephthalate film support:

- (1) magenta dye-releasing Compound IX (22 mg./ft.²) and gelatin (200 mg./ft.²),
- (2) green-sensitive, negative, gelatin-silver bromiodide emulsion (80 mg. gelatin/ft.² and 108 mg. silver/ft.²),
- (3) scavenger interlayer of gelatin (80 mg./ft.²) and 1-

24

(2',4',6' - trichlorophenyl) - 3 - [3'' - (2''',4'''-diamylphenoxyacetamido)benzamido] - 4 - (p - methoxyphenylazo)-5-pyrazolone (75 mg./ft.²),

- (4) yellow dye-releasing Compound VI (77 mg./ft.²) and gelatin (200 mg./ft.²) and
- (5) blue-sensitive, negative, gelatin-silver bromiodide emulsion (160 mg. gelatin/ft.² and 216 mg. silver/ft.²) and piperidino hexose reductone (10 mg./ft.²).

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 dye image-receiving element prepared as in Example 3 by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers at a gap of 0.004 inch:

	G.
Hydroxyethyl cellulose	2.5
Sodium hydroxide	0.75
Potassium bromide	0.50
Anhydrous sodium sulfite	1.60
Hydroquinone	0.25
p-Methylaminophenol	0.25
Water to 100 g.	

After 60 seconds at about 20° C., the film unit is separated and a well-defined yellow dye image is observed in the blue exposure region while a well-defined magenta dye image is observed in the green exposure region. A well-defined red dye image is observed from the region of the negative exposed to both blue and green light.

EXAMPLE 5

A multilayer, multicolor, photosensitive element is prepared by coating the following layers in the order recited on a polyethylene terephthalate film support:

- (1) magenta dye-releasing Compound VIII (20 mg./ft.²) and gelatin (200 mg./ft.²),
- (2) green-sensitive, negative, gelatin-silver bromiodide emulsion (80 mg. gelatin/ft.² and 108 mg. silver/ft.²),
- (3) scavenger interlayer of gelatin (104 mg./ft.²), 1-(2',4',6'-trichlorophenyl) - 3 - [3'' - (2''',4'''-diamylphenoxyacetamido) - benzamido] - 4 - (p - methoxyphenylazo) - 5 - pyrazolone (75 mg./ft.²), dioctylhydroquinone (20 mg./ft.²) and 4'-methylphenylhydroquinone (20 mg./ft.²),
- (4) yellow dye-releasing Compound VI (77 mg./ft.²) and gelatin (200 mg./ft.²) and
- (5) blue-sensitive, negative, gelatin-silver bromiodide emulsion (160 mg. gelatin/ft.² and 216 mg. silver/ft.²).

A multilayer image-receiving element is prepared by coating the following layers in the order recited on a polyethylene-coated paper support:

- (1) tri-n-octylpropylammonium bromide (151 mg./ft.²), methyl - tri - n - dodecylammonium p-toluenesulfonate (22.6 mg./ft.²) and gelatin (637 mg./ft.²) and
- (2) gelatin overcoat (100 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 the superposed dye image-receiving element by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers at a gap of 0.004 inch:

	G.
Hydroxyethyl cellulose	2.50
Sodium hydroxide	0.75
Potassium bromide	0.50
Piperidino hexose reductone	0.15
Distilled water to 100 g.	

After 60 seconds at about 20° C., the film unit is separated and a well-defined, negative, yellow dye image is observed in the blue exposure region while a well-defined negative magenta dye image is observed in the green ex-

25

posure region. A well-defined red dye image is observed from the region of the negative exposed to both blue and green light. The following sensitometric data is obtained from the negative dye images present on the image-receiving element:

	Density		
	R	G	B
Blue.....	0.15	0.44	0.56
Green.....	0.17	0.57	0.36
Clear.....	0.17	0.58	0.57

EXAMPLE 6

This example demonstrates the effect that sulfite ion has upon dye images when present in the developer composition.

A multilayer photosensitive element is prepared by coating the following layers in the order recited on a polyethylene terephthalate film support:

- (1) yellow dye-releasing Compound VII (68 mg./ft.²) and gelatin (400 mg./ft.²) and
- (2) blue-sensitive, negative, gelatin-silver bromide emulsion (160 mg. gelatin/ft.² and 200 mg. silver/ft.²) and piperidino hexose reductone (20 mg./ft.²).

The photosensitive element is exposed to a graduated-density, multicolor test object. A dye image-receiving element prepared as in Example 2 is dipped for 15 seconds in the following activator solution and then laminated to the above multilayer photosensitive element:

Sodium hydroxide	G.
Potassium bromide	0.40
Distilled water to 100 g.	0.50

After 60 seconds at about 20° C., the film unit is separated and a faint negative yellow dye image is observed on the image-receiving element.

Another sample of the above photosensitive element is exposed and laminated in the same fashion to another sample of the dye image-receiving element prepared as in Example 2 which has been dipped for 15 seconds in the following activating composition:

Sodium hydroxide	G.
Potassium bromide	0.40
Sodium sulfite	0.50
Distilled water to 100 g.	1.60

After 60 seconds at about 20° C., the film unit is separated and a marked improvement in negative dye image discrimination is observed on the dye image-receiving element which is attributable to the presence of sulfite ion in the activating composition.

When the above procedure is repeated except for substituting an equimolar amount of sodium sulfate (1.80 g./100 g. composition) for sodium sulfite in the activating composition, no marked improvement in negative dye image discrimination is observed.

EXAMPLE 7

This example illustrates the use of a direct-positive emulsion to obtain a direct-positive dye image.

A multilayer direct-positive photosensitive element is prepared by coating the following layers in the order recited on a polyethylene terephthalate film support:

- (1) yellow dye-releasing Compound VI (77 mg./ft.²), piperidino hexose reductone (40 mg./ft.²) and gelatin (400 mg./ft.²) and
- (2) gelatin-silver chlorobromide emulsion (160 mg. gelatin/ft.² and 216 mg. silver/ft.²) and fogging agent 2,3 - dimethyl-6-nitrobenzoselenazolium p-toluenesulfonate (400 mg./mole silver).

26

A sample of the photosensitive element is exposed to a graduated-density multi-color 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 prepared as in Example 2 by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers at a gap of 0.005 inch:

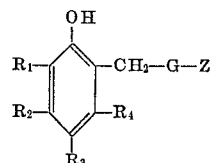
Hydroxyethyl cellulose	G.
Sodium hydroxide	2.50
Potassium bromide	0.40
Sodium sulfite	0.50
Hydroquinone	1.60
Distilled water to 100 g.	0.18

After 60 seconds at about 20° C., the film unit is separated and a well-defined positive, yellow dye image is observed on the dye image-receiving element.

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.

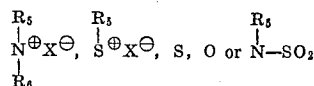
We claim:

1. A 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, said compound having the formula:



wherein:

- R₁ represents hydrogen, an hydroxy group, an amino group, an alkyl group or an aryl group;
- R₂ and R₄ each represents hydrogen, an alkyl group or an aryl group;
- R₃ represents hydrogen, an hydroxyl group, an alkyl group or an aryl group, with the proviso that when R₁ represents hydrogen, an alkyl group or an aryl group, R₃ must represent an hydroxyl group;
- G represents:



wherein R₅ and R₆ each represents an alkyl group, an aryl group, or, when R₅ and R₆ are taken together with the nitrogen to which they are connected, represent a divalent pyridinium group, and X[⊖] represents an acidic anion;

Z represents a moiety which in combination with G forms a dye image-providing material which is a dye or dye precursor; and

at least one of R₁, R₂, R₃, R₄ or G—Z being a ballast-ing radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline medium.

2. The photosensitive element of claim 1 wherein:

- R₁ represents hydrogen,
- R₂ represents an alkyl group,
- R₃ represents an hydroxyl group,
- R₄ represents hydrogen, and
- G represents:



wherein R_5 and R_6 each represents a methyl group or, when taken together with the nitrogen to which they are attached, represent a divalent pyridinium group, and $X^\ominus$ represents an acidic anion.

3. The photosensitive element of claim 1 wherein R_2 is an alkyl group of 8 to 20 carbon atoms.

4. 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, said compound being:

anhydro - 3 - (2 - amino-3,6-disulfo-1-naphthylazo)-1-(4 - n - dodecyl - 2,5 - dihydroxybenzyl)pyridinium hydroxide (inner salt) or

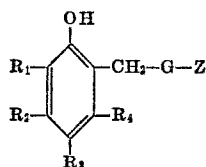
anhydro - 3 - (2 - amino - 3,6 - disulfo-1-naphthylazo)-
1 - (4 - t - octyl - 2,5-dihydroxybenzyl)pyridinium hy- 15
droxide (inner salt) or

anhydro - N - [4 - (8-amino - 1 - hydroxy-3,6-disulfo-2-naphthylazo)benzyl] - N - (4-t-octyl - 2,5-dihydroxybenzyl)-dimethylammonium hydroxide (inner salt) 20
or

anhydro - N - [3 - (2,3-dihydro-3-methyl-2-oxo-1-sul-
fophenyl-3-azabenzanthron - 6 - yl amino)propyl]-N-
(2,5 - dihydroxy-4-methylbenzyl)-N,N-dimethylam-
monium hydroxide (inner salt) or

anhydro - N - [4-(8-amino - 1 - hydroxy-3,6-disulfo-2-naphthylazo)benzyl] - N - (4 - n - dodecyl-2,5-dihydroxybenzyl)-dimethylammonium hydroxide (inner salt)

5. 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, said compound having the formula:



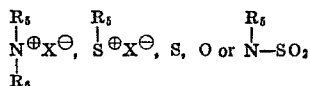
wherein:

R₁ represents hydrogen, an hydroxyl group, an amino group, an alkyl group or an aryl group; 50

R_2 and R_4 each represents hydrogen, an alkyl group or an aryl group;

R_3 represents hydrogen, an hydroxyl group, an alkyl group or an aryl group, with the proviso that when R_1 represents hydrogen, an alkyl group or an aryl group, R_3 must represent an hydroxyl group;

G represents:



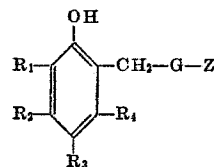
wherein R₅ and R₆ each represents an alkyl group, an aryl group or, when R₅ and R₆ are taken together with the nitrogen to which they are connected, represent a divalent pyridinium group, and X[⊖] represents an acidic anion;

Z represents a moiety which in combination with G forms a dye image-providing material which is a dye or dye precursor; and

at least one of R₁, R₂, R₃, R₄ or G—Z being a ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline medium.

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, said compound having the formula:

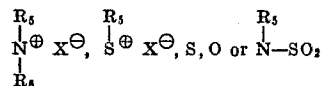


wherein:

R₁ represents hydrogen, an hydroxyl group, an amino group, an alkyl group or an aryl group; R₂ and R₄ each represents hydrogen, an alkyl group or an aryl group;

R₃ represents hydrogen, an hydroxyl group, an alkyl group or an aryl group, with the proviso that when R₁ represents hydrogen, an alkyl group or an aryl group, R₃ must represent an hydroxyl group:

G represents:



wherein R₅ and R₆ each represents an alkyl group, an aryl group or, when R₅ and R₆ are taken together with the nitrogen to which they are connected, represent a divalent pyridinium group, and X[⊖] represents an acidic anion;

Z represents a moiety which in combination with G forms a dye image-providing material which is a dye or dye precursor; and

at least one of R_1 , R_2 , R_3 , R_4 or $G-Z$ being a ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline medium;

(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:

R₁ represents hydrogen,
R₂ represents an alkyl group,
R₃ represents a hydroxyl group,
R₄ represents hydrogen and
G represents:



wherein R_5 and R_6 each represents a methyl group or, when taken together with the nitrogen to which they are attached, represent a divalent pyridinium group, and $X^\ominus$ represents an acidic anion.

8. The film unit of claim 7 wherein R₂ is an alkyl group of 8 to 20 carbon atoms.

9. The film unit of claim 6 wherein said processing
75 composition contains sulfite ions.

29

10. 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, said compound being:

anhydro-3-(2-amino-3,6-disulfo-1-naphthylazo)-1-(4-n-dodecyl-2,5-dihydroxybenzyl)pyridinium hydroxide (inner salt) or
 anhydro-3-(2-amino-3,6-disulfo-1-naphthylazo)-1-(4-t-octyl-2,5-dihydroxybenzyl)pyridinium hydroxide (inner salt) or
 anhydro-N-[4-(8-amino-1-hydroxy-3,6-disulfo-2-naphthylazo)benzyl]-N-(4-t-octyl-2,5-dihydroxybenzyl)dimethylammonium hydroxide (inner salt) or
 anhydro-N-[3-(2,3-dihydro-3-methyl-2-oxo-1-sulphophenyl-3-azabenzanthron-6-ylamino)propyl]-N-(2,5-dihydroxy-4-methylbenzyl)-N,N-dimethylammonium hydroxide (inner salt) or
 anhydro-N-[4-(8-amino-1-hydroxy-3,6-disulfo-2-naphthylazo)benzyl]-N-(4-n-dodecyl-2,5-dihydroxybenzyl)dimethylammonium hydroxide (inner salt);

- (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.

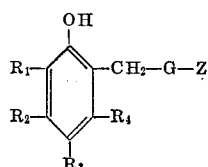
11. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

- (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 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;

- (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;

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



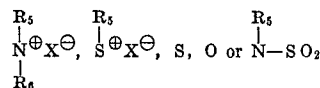
wherein:

- R₁ represents hydrogen, an hydroxyl group, an amino group, an alkyl group or an aryl group;
 R₂ and R₄ each represents hydrogen, an alkyl group or an aryl group;
 R₃ represents hydrogen, an hydroxyl group, an alkyl group or an aryl group, with the proviso that when

30

R₁ represents hydrogen, an alkyl group or an aryl group, R₃ must represent an hydroxyl group;

G represents:



wherein R₅ and R₆ each represents an alkyl group, an aryl group or, when R₅ and R₆ are taken together with nitrogen to which they are connected, represent a divalent pyridinium group, and X[⊖] represents an acidic anion;

Z represents a moiety which in combination with G forms a dye image-providing material which is a dye or dye precursor; and

at least one of R₁, R₂, R₃, R₄ or G—Z being a ballast-ing radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline medium;

20 said film unit containing a silver halide developing agent.

12. The film unit of claim 11 wherein said dye image-receiving layer is located in said photosensitive element between said support and the lowermost photosensitive silver halide emulsion layer.

25 13. The film unit of claim 11 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.

30 14. The film unit of claim 13 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.

15. The film unit of claim 11 wherein:

- R₁ represents hydrogen,
 R₂ represents an alkyl group;
 R₃ represents an hydroxyl group;
 R₄ represents hydrogen and
 G represents:

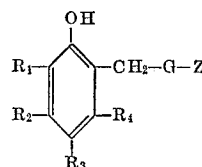


wherein R₅ and R₆ each represents a methyl group or, when taken together with the nitrogen to which they are attached, represent a divalent pyridinium group, and X[⊖] represents an acidic anion.

16. The film unit of claim 15 wherein R₂ is an alkyl group of from 8 to 20 carbon atoms.

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

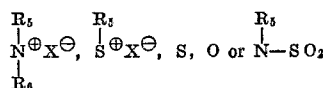


wherein:

- R₁ represents hydrogen, an hydroxyl group, an amino group, an alkyl group or an aryl group;
 R₂ and R₄ each represents hydrogen, an alkyl group or an aryl group;
 R₃ represents hydrogen, an hydroxyl group, an alkyl group or an aryl group, with the proviso

31

that when R_1 represents hydrogen, an alkyl group or an aryl group, R_3 must represent an hydroxyl group;
G represents:



wherein R_5 and R_6 each represents an alkyl group, an aryl group or, when R_5 and R_6 are taken together with the nitrogen to which they are connected, represent a divalent pyridinium group, and $X^{\ominus}$ represents an acidic anion;

Z represents a moiety which in combination with G forms a dye image-providing material which is a dye or dye precursor; and

at least one of R_1 , R_2 , R_3 , R_4 or G—Z being a ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline medium;

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

(c) said oxidized developing agent thereby cross-oxidizing said cleavable compound to cause said compound to cleave, thus forming an imagewise distribution of diffusible dye 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 diffusing to a dye image-receiving layer.

18. The process of claim 17 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 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.

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

anhydro-3-(2-amino-3,6-disulfo-1-naphthylazo)-1-(4-n-dodecyl-2,5-dihydroxybenzyl)pyridinium hydroxide (inner salt) or

anhydro-3-(2-amino-3,6-disulfo-1-naphthylazo)-1-(4-t-octyl-2,5-dihydroxybenzyl)pyridinium hydroxide (inner salt) or

anhydro-N-[4-(8-amino-1-hydroxy-3,6-disulfo-2-naphthylazo)benzyl]-N-(4-t-octyl-2,5-dihydroxybenzyl)dimethylammonium hydroxide (inner salt) or

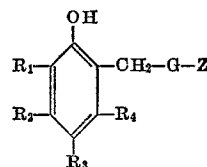
anhydro-N-[3-(2,3-dihydro-3-methyl-2-oxo-1-sulfo-phenyl-3-azabenzanthron-6-ylamino)propyl]-N-(2,5-dihydroxy-4-methylbenzyl)-N,N-dimethylammonium hydroxide (inner salt) or

anhydro-N-[4-(8-amino-1-hydroxy-3,6-disulfo-2-naphthylazo)benzyl]-N-(4-n-dodecyl-2,5-dihydroxybenzyl)dimethylammonium hydroxide (inner salt)

32

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

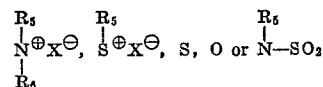


wherein:

R_1 represents hydrogen, an hydroxyl group, an amino group, an alkyl group or an aryl group;
 R_2 and R_4 each represents hydrogen, an alkyl group or an aryl group;

R_3 represents hydrogen, an hydroxyl group, an alkyl group or an aryl group, with the proviso that when R_1 represents hydrogen, an alkyl group or an aryl group, R_3 must represent an hydroxyl group;

G represents:



wherein R_5 and R_6 each represents an alkyl group, an aryl group or, when R_5 and R_6 are taken together with the nitrogen to which they are connected, represent a divalent pyridinium group, and $X^{\ominus}$ represents an acidic anion;

Z represents a moiety which in combination with G forms a dye image-providing material which is a dye or dye precursor; and

at least one of R_1 , R_2 , R_3 , R_4 or G—Z being a ballasting radical of such molecular size and configuration as to render said cleavable compound nondiffusible during development in an alkaline medium;

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

(c) said oxidized developing agent thereby cross-oxidizing each said cleavable compound to cause each said compound to cleave, thus forming an imagewise distribution of diffusible dye as a function of said imagewise exposure of each of said silver halide emulsion layers.

21. The process of claim 20 wherein:

R_1 represents hydrogen,
 R_2 represents an alkyl group,
 R_3 represents an hydroxyl group,
 R_4 represents hydrogen and
G represents:



33

wherein R_5 and R_6 each represents a methyl group or, when taken together with the nitrogen to which they are attached, represent a divalent pyridinium group, and $X^\ominus$ represents an acidic anion.

22. The process of claim 21 wherein R_2 is an alkyl group of from 8 to 20 carbon atoms.

34

NORMAN G. TORCHIN, Primary Examiner

A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

96—29 D, 76 R, 76 C, 77

References Cited**UNITED STATES PATENTS**

3,364,022 1/1968 Barr 96—3