United States Patent [19]
Lestina et al.

[11] **3,880,658**
[45] **Apr. 29, 1975**

[54] PHOTOGRAPHIC ELEMENTS CONTAINING OXICHROMIC COMPOUNDS WITH REDUCED AZOMETHINE LINKAGES

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

[22] Filed: **Nov. 22, 1972**

[21] Appl. No.: **308,869**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 206,836, Dec. 10, 1971, abandoned.

[52] **U.S. Cl.** .... **96/29 D;** 96/3; 96/77; 96/99

[51] **Int. Cl.** **G03c 7/00;** G03c 5/54; G03c 1/40; G03c 1/10

[58] **Field of Search** .... 96/3, 29 D, 77, 99

[56] **References Cited**

UNITED STATES PATENTS

3,065,074	11/1962	Rogers	96/3
3,227,550	1/1966	Whitmore et al.	96/3
3,227,551	1/1966	Barr et al.	96/3
3,230,082	1/1966	Land et al.	96/3
3,255,001	6/1966	Blout et al.	96/3
3,260,597	7/1966	Weyerts et al.	96/3
3,320,063	5/1967	Bloom	96/77
3,347,671	10/1967	Salimen	96/3
3,415,644	12/1969	Land	96/3
3,537,850	11/1970	Simon	96/3
3,698,897	10/1972	Gampf et al.	96/3
3,725,062	4/1973	Anderson et al.	96/3
3,728,113	4/1973	Becker et al.	96/3

Primary Examiner—Norman G. Torchin
Assistant Examiner—Richard L. Schilling
Attorney, Agent, or Firm—G. E. Battist

[57] ABSTRACT

Oxichromic compounds are disclosed, along with photographic compositions and photographic elements containing oxichromic compounds. In one aspect, the oxichromic compounds are those compounds which undergo chromogenic oxidation to form the chromophore of an imine image dye. In another aspect, photographic elements are disclosed which contain a photosensitive composition having associated therewith an oxichromic developer; preferably, the photographic elements are used in image transfer film units. In another aspect, photographic elements are disclosed which contain a photosensitive composition having associated therewith a nondiffusible compound containing an oxichromix moiety which splits off to form a diffusible oxichromic moiety when contacted with an oxidized silver halide developer.

75 Claims, 7 Drawing Figures

FIG. 1

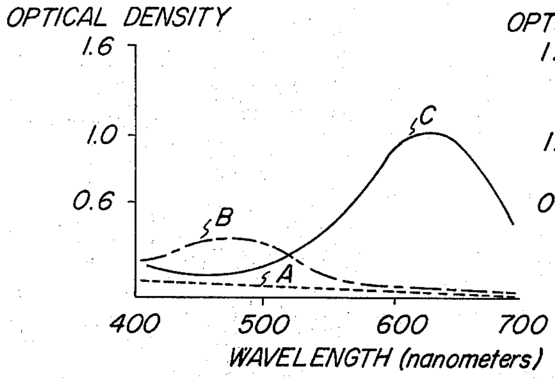
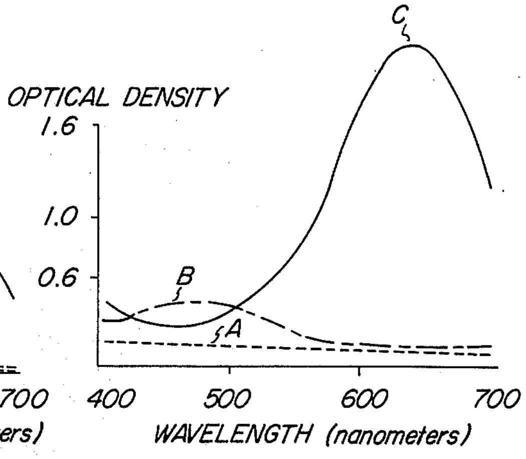


FIG. 2



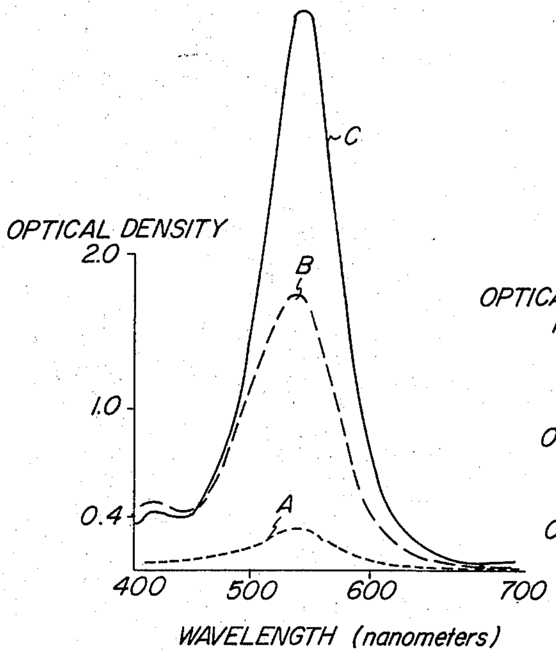


FIG. 3

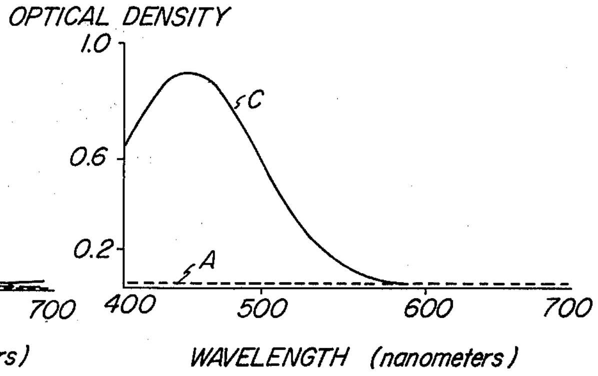


FIG. 4

FIG. 5

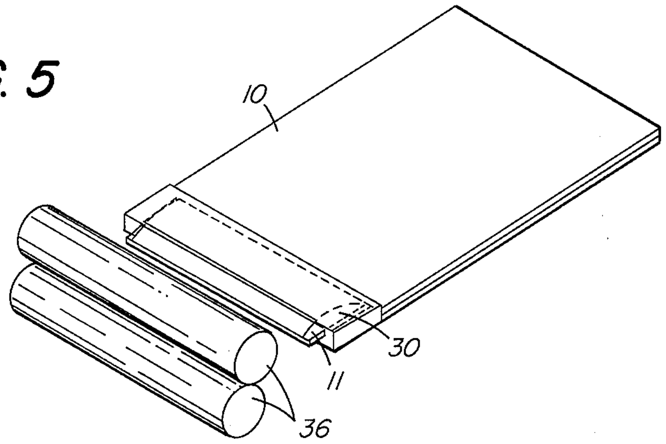


FIG. 6

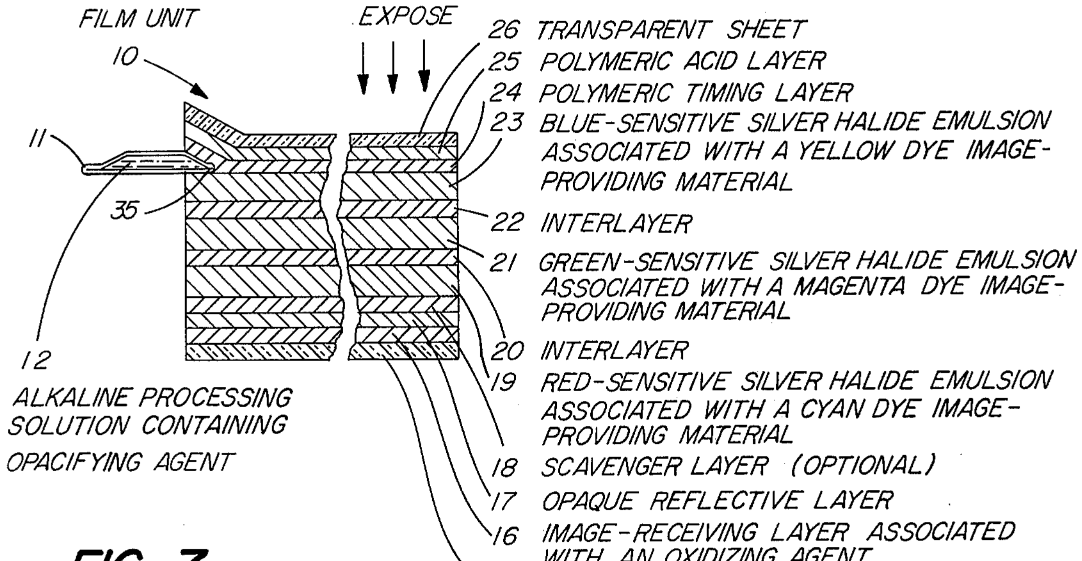
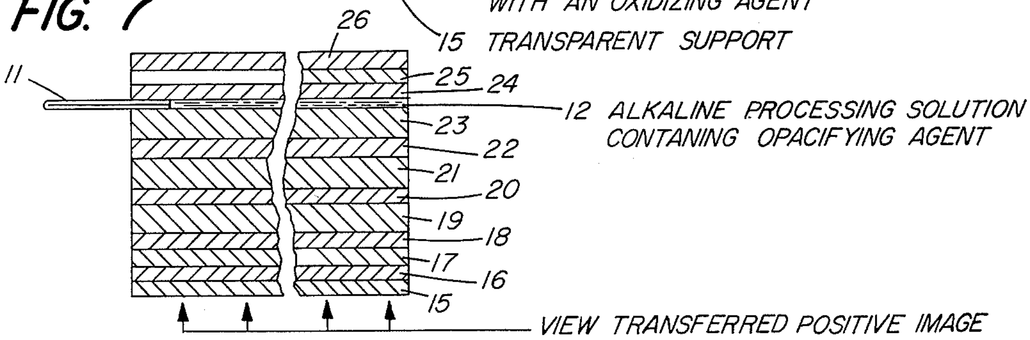


FIG. 7



PHOTOGRAPHIC ELEMENTS CONTAINING OXICHROMIC COMPOUNDS WITH REDUCED AZOMETHINE LINKAGES

This application is a continuation-in-part of U.S. Ser. No. 206,836 filed Dec. 10, 1971, now abandoned.

This invention relates to photographic elements containing oxichromic compounds and processes for forming photographic images in these elements. In one aspect, this invention relates to photographic elements containing oxichromic developers which are compounds which contain a moiety which is a silver halide developer linked to a moiety which is a precursor for an indophenol. In another aspect, this invention relates to photographic elements containing oxichromic developers which can be oxidized to form the imine chromophore of azomethine (imine) compounds. In another aspect, this invention relates to a photographic element comprising a nondiffusing compound which releases a diffusible oxichromic precursor for an azomethine dye upon contact with an oxidized silver halide developer. In still another aspect, this invention relates to photographic elements containing oxichromic compounds wherein the dye-forming moiety is stabilized to prevent premature oxidation.

It is known in the art to use leuco developing agents in photographic transfer elements which, upon reaction to reduce silver halide to silver, will produce a chromophore between the developing moiety and groups attached directly thereto, as disclosed in U.S. Pat. Nos. 2,992,105 and 2,909,430. There are disclosures in the art of dye developers wherein a developing moiety is linked directly to a preformed dye, for example, in U.S. Pat. Nos. 2,983,606, 3,255,001, etc. There are also disclosures of image transfer systems wherein a nondiffusing compound releases a preformed dye upon contact with an oxidized color developing agent, as disclosed in Whitmore, U.S. Pat. No. 3,227,552. Moreover, leuco compounds which reduce silver halide to silver and are in turn oxidized by the reaction to provide a colored compound having a chromophore are known, as evidenced by U.S. Pat. Nos. 1,102,028 by Fischer issued June 30, 1914, and 2,206,126 by Schinzel issued July 2, 1940. However, the leuco dye systems known in the art did not find general commercial acceptance in color photography because of their poor properties as developing agents and dyes, as disclosed in Hunt, *The Reproduction of Colors*, 1967, page 291.

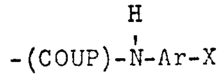
We have now discovered new classes of compounds and improved photographic systems which in one embodiment provide more design latitude in making an image transfer film unit and provide improved photographic and image characteristics in the element. Generally, the new compounds which can be used in the image transfer film units are those which contain a moiety which can undergo chromogenic oxidation to form an azomethine chromophore or imine chromophore. In certain embodiments, the oxidized compounds provide the desired image dye; however, when indophenols are formed, it is preferred to contact the indophenol with an 'onium compound to provide an 'onium indophenoxide image dye.

In one preferred embodiment, this invention relates to photographic elements containing a photosensitive substance and having associated therewith an oxichromic compound, i.e., a compound which undergoes chromogenic oxidation to form a new chromophore. In one preferred embodiment, the oxichromic compounds

are the oxichromic developers which contain a developing moiety and an oxichromic moiety and have the general formula:

$$D-(OC)$$

wherein D is a group which is a silver halide developer including developers containing hydrolyzable groups thereon, and is generally an aromatic group which is preferably disubstituted containing at least two substituents thereon which can be hydroxyl groups or hydrolyzable derivatives thereof, primary amine groups, or alkylamino groups including substituted alkylamino groups, and (OC) is a moiety which undergoes chromogenic oxidation to form an azomethine or imine image dye and is preferably represented by the structure



$$-(COUP)-\overset{H}{N}-Ar-X$$

wherein COUP is a photographic color-forming coupler linked to said nitrogen atom through a carbon atom at the coupling position, such as, for example, a phenolic coupler, a pyrazolone coupler, a pyrazolotriazole coupler, couplers having open-chain active methylene groups and the like, and preferably soluble couplers which have solubilizing groups attached thereto to provide a diffusible coupler, and the like; Ar is an arylene group containing from about 6 to about 20 carbon atoms, including substituted and unsubstituted arylene groups, fused-ring arylene groups and the like, and is preferably a phenylene group which is preferably substituted with halogen atoms or groups containing halogen atoms in the ortho or meta position of the ring; and X can be an amino group, including substituted amines, or preferably is an hydroxyl group. Generally, in this embodiment the oxichromic developer is initially diffusible or processing-composition-soluble and will migrate to an image-receiving layer unless the developer group is oxidized by reaction with developable silver halide or oxidized with a redox agent; the image-receiving layer preferably has an oxidizing agent associated therewith to provide for the chromogenic oxidation of the oxichromic compound. Further details on coupler definitions are found in U.S. Pat. No. 3,620,747 issued Nov. 16, 1971, now U.S. Pat. No. 3,791,827 and in Bush et al, U.S. Ser. No. 169,706 filed Aug. 6, 1971, both of which are incorporated herein by reference.

In another embodiment, this invention relates to image transfer elements containing compounds represented by the formula:

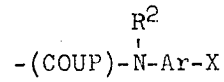
$$D-(OC)$$

wherein D and (OC) are as defined above, and also to processes for forming image records in these image transfer elements.

In another highly preferred embodiment, this invention relates to image transfer systems which comprise a silver halide emulsion having associated therewith an oxichromic developer, an image-receiving layer and an 'onium salt. The chromophore of the oxichromic developer can be formed by aerial oxidation or formed by oxidation with an oxidizing agent which is in association with the image-receiving layer.

In another embodiment of this invention, an image transfer system contains an immobile or nondiffusible compound which contains the oxichromic moiety defined as (OC) above. An oxichromic moiety having substantially lower molecular weight than the immobile compound is released or made diffusible by reaction of the compound with a silver halide developing agent such as by a redox reaction or by coupling reactions with color developers such as the aromatic primary amines.

In a highly preferred embodiment, this invention relates to photographic elements containing stabilized oxichromic compounds which are highly resistant to premature oxidation. Useful stabilized oxichromic compounds contain the group:

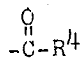


$$-(COUP)-\overset{R^2}{\overset{|}{N}}-Ar-X$$

wherein (COUP), Ar and X are as defined above, with the provision that X can also be the group:

$$—O—R^1$$

wherein R^1 is a carbonyl-containing group such as a group of the formula:



$$-\overset{O}{\overset{\|}{C}}-R^4$$

wherein R^4 is an acyl group such as a group containing 1 to 12 carbon atoms which can be an alkyl group, an aryl group, a substituted alkyl group or a substituted aryl group, and R^2 is a hydrogen atom or the same substituent as R^1, provided that at least one of R^1 and R^2 is a carbonyl-containing group. In one highly preferred embodiment, R^1 and R^2 are trifluoroacetyl groups. In this embodiment, the oxichromic compound can undergo a base catalyzed oxidation wherein stabilizing groups R^2 and/or R^1 are hydrolyzed by a strong base to permit oxidation to occur. Preferably, R^4 is an alkyl group having 1–4 carbon atoms and is preferably halogen-substituted. The stabilized oxichromic moieties can, of course, be linked to a nondiffusible coupler or linked to a developing moiety for use in a photographic system.

In another highly preferred embodiment, this invention relates to image transfer elements comprising the combination of an oxichromic compound an incorporated auxiliary silver halide developer such as a pyrazolidone developer.

In still another embodiment, this invention relates to image transfer elements comprising the combination of an oxichromic compound and an inhibitor-releasing developer.

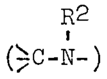
The group defined as Ar above is preferably the residue of an aromatic color developing agent such as an aminophenol, a phenylenediamine and the like and, of course, including the various substituents on the aromatic group which are known in the art for the respective color developing agent. In one preferred embodiment where Ar is the nucleus of an aminophenol developing agent, it can contain the same substituents as disclosed, for example, on the aminophenol developing agents disclosed in Bush et al, U.S. Ser. No. 169,706 filed Aug. 6, 1971, now U.S. Pat. No. 3,791,827 which is incorporated herein by reference.

In the above compounds where a developing agent moiety (D) is connected to an oxichromic moiety, the oxichromic moiety preferably contains an insulating linkage connecting it to the developing agent moiety (D). Insulating linkages of this type, sometimes referred to as achromophoric groups or bonds, are known in the art, for example, as disclosed in U.S. Pat. No. 3,255,001 issued June 7, 1966. The insulating group does not contribute a color-producing group to the dye formed upon chromogenic oxidation, but acts to prevent or interrupt any system of conjugation or resonance extending from the azomethine groups formed in the oxichromic moiety to the developing group, i.e., such as a hydroquinone group. Thus, any influence of the developer group on the color characteristics of the azomethine linkage is substantially excluded. The insulating linkage which preferably forms a part of the oxichromic moiety as defined herein can be any group which will break up the resonance system, for example, those groups listed in U.S. Pat. No. 3,255,001 issued June 7, 1966, and the like.

The term "azomethine linkage" as used herein is understood to mean the grouping:

$$(>C{=}N-)$$

which is more commonly referred to in the chemical literature as an "imine" group and is exclusive of hydrogen atom substitution. The oxichromic compounds of this invention contain a group which undergoes oxidation to form an imine group which is understood to be the chromophore of the imine image dyes or azomethine image dyes as referred to herein. The term "reduced azomethine linkage" or "reduced imine linkage" is understood to mean the grouping:



$$(\geq C-\overset{R^2}{\overset{|}{N}}-)$$

wherein R^2 is as previously defined. In certain preferred embodiments, the azomethine compounds of this invention are further defined as being indophenols, which is understood to refer to compounds containing a group having the general structure:

$$(COUP)=N—Ar—OH$$

wherein (COUP) is a color coupler such as pyrazolone color coupler, a pyrazolotriazole coupler, an open-chain ketomethylene color coupler, a phenolic color coupler and the like, which is connected to the nitrogen atom in the coupling position of said coupler; and Ar is as defined above.

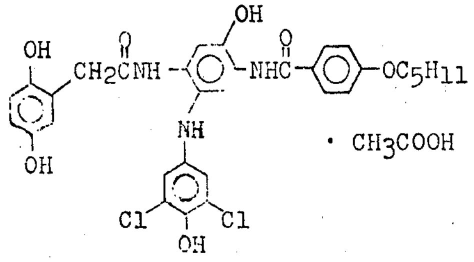
The term "nondiffusing" used herein has the meaning commonly applied to the term in color photography and denotes materials which for all practical purposes do not migrate or wander through organic colloid layers, such as gelatin, comprising the sensitive elements of the invention. The same meaning is to be attached to the term "immobile."

The term "diffusible" as applied to the color-providing materials of this invention has the converse meaning and denotes materials having the property of diffusing effectively through the colloid layers of the sensitive elements in the presence of "nondiffusing" materials. "Mobile" has the same meaning.

The oxichromic compounds which provide very useful image transfer systems include those compounds which are diffusible in an alkaline solution which generally have the formula:

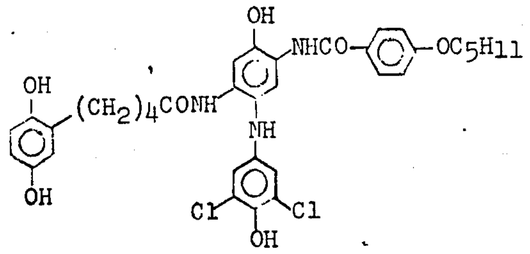
$$D—(OC)$$

wherein D and (OC) are defined as above. Typical representative compounds of this type are as follows:



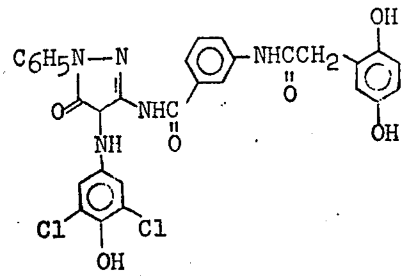
Compound I

m.p. 225-227° C.



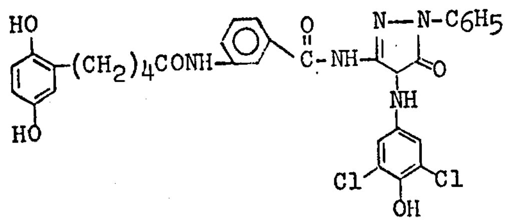
Compound II

m.p. 219-222° C.



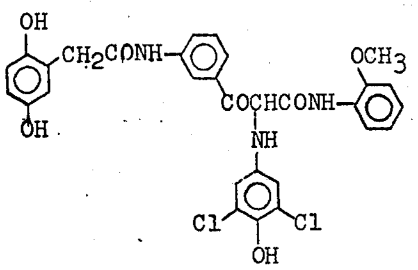
Compound III

m.p. 170-176° C.



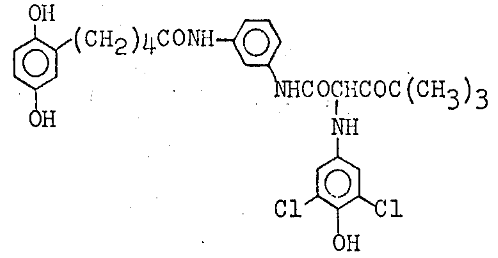
Compound IV

m.p. 130-150° C.



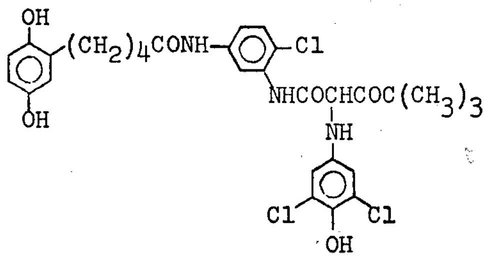
Compound V

m.p. 134-137° C.



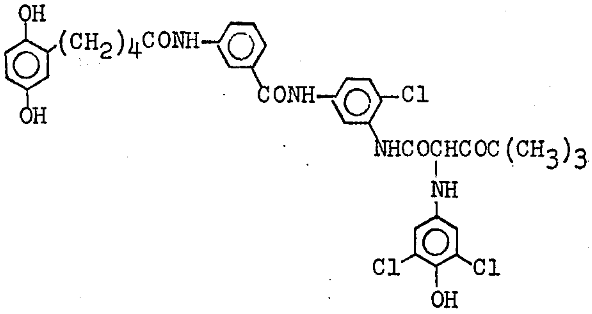
Compound VI

m.p. 90° C.



Compound VII

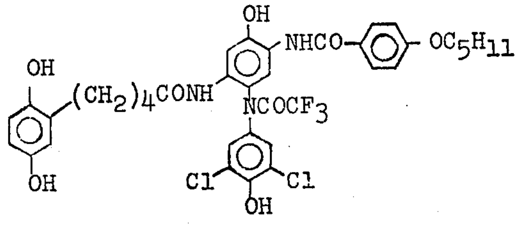
m.p. 92-96° C.



Compound VIII

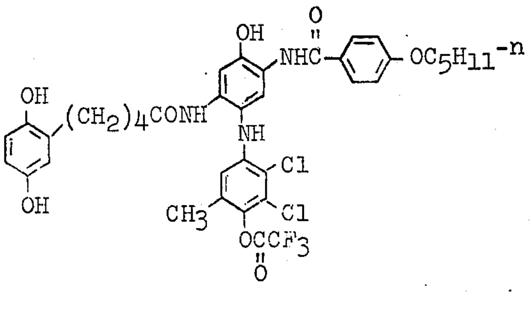
m.p. 115° C.

Some of the stabilized compounds according to this invention which can be effectively used as oxichromic developing agents in image transfer systems include:

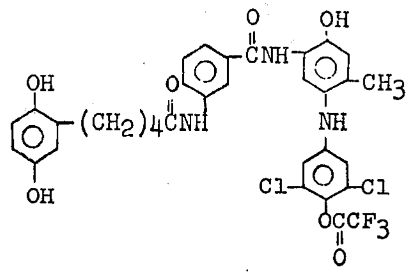


m.p. 171-173° C.

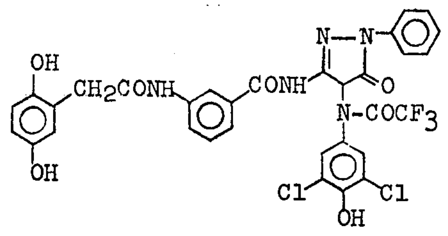
Compound IX



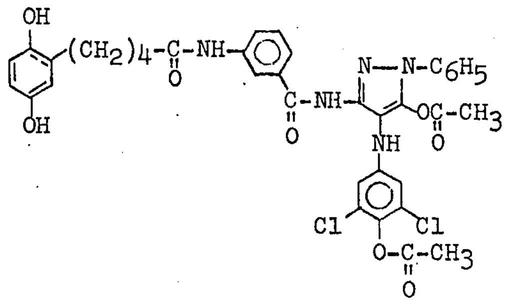
Compound X



Compound XI

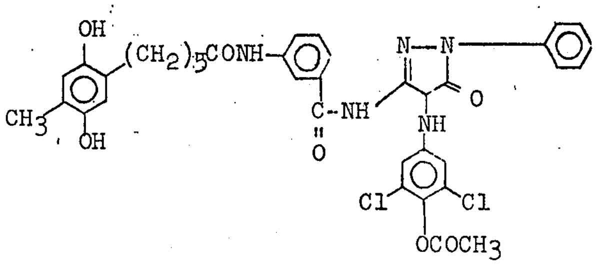


Compound XII

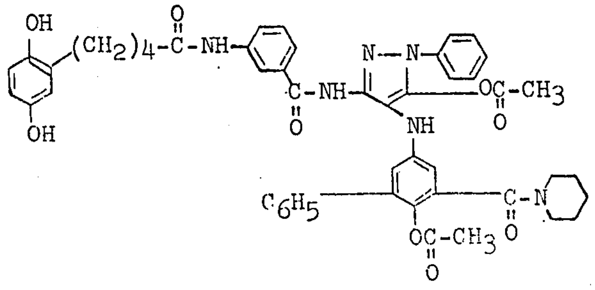


m.p. 80° C.

Compound XIII

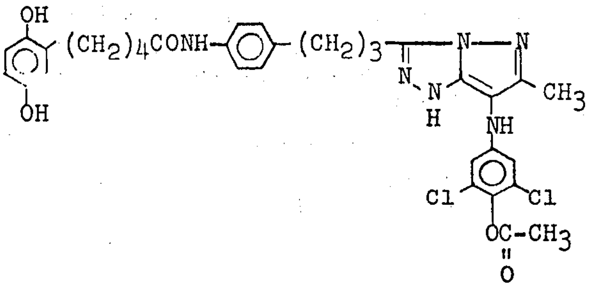


Compound XIV



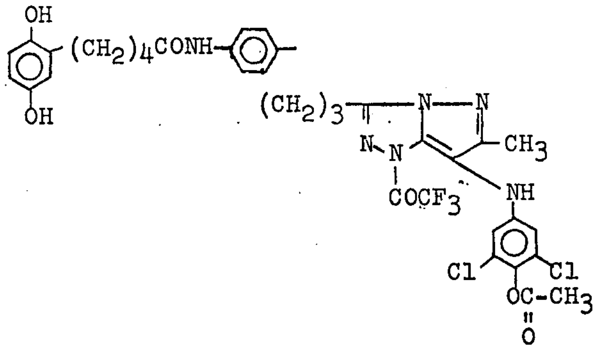
m.p. 110-117° C.

Compound XV

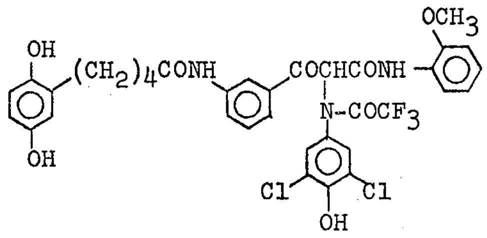


m.p. 112-114° C.

Compound XVI

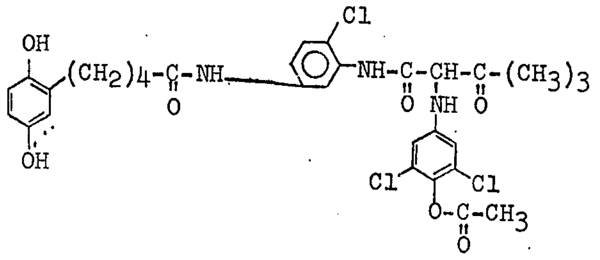


Compound XVII



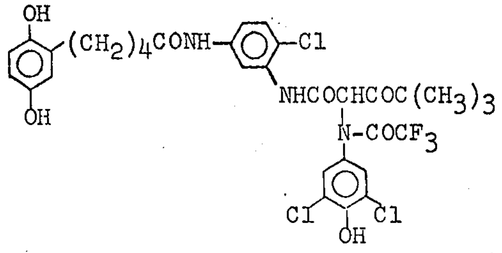
m.p. 90-95° C. (dec.)

Compound XVIII



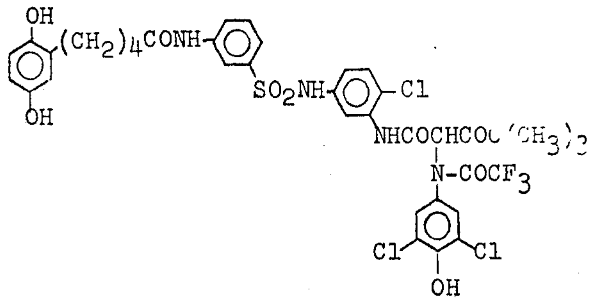
m.p. 78-80° C.

Compound XIX



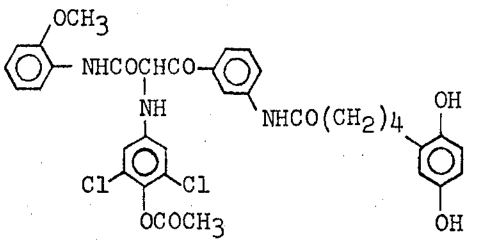
Compound XX

m.p. 215-216° C.



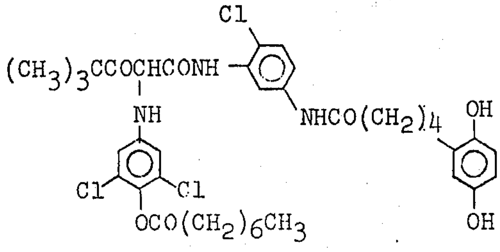
m.p. 131-136° C.

Compound XXI



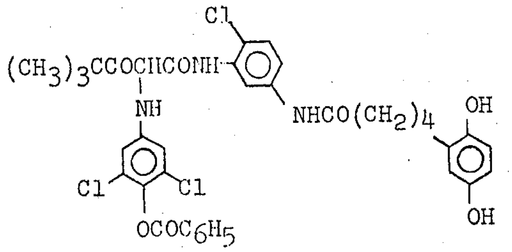
m.p. 120-130° C. dec.

Compound XXII



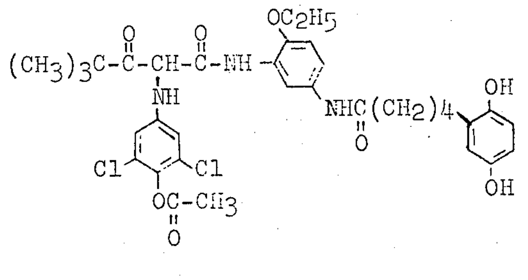
m.p. 90° C.

Compound XXIII

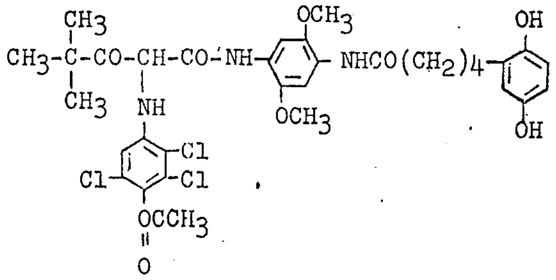


m.p. 120° C.

Compound XXIV

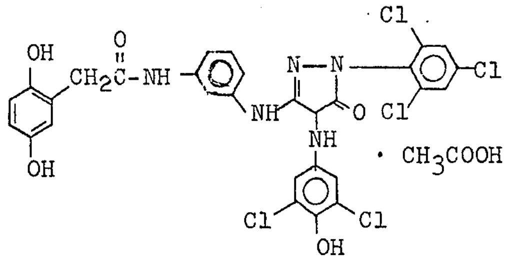


Compound XXV



Compound XXVI

The salts of the oxichromic compounds do provide some additional stability, but they are generally not as stable as the acylated compounds next above. A typical salt of an oxichromic compound is as follows:



m.p. 177-180° C.

Compound XXVII

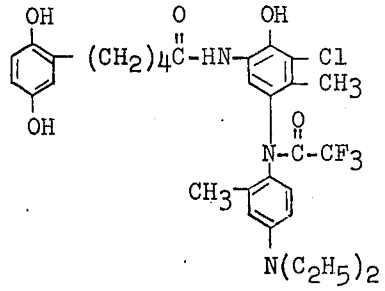
The oxichromic compounds described above can be prepared by the procedures described in Lestina and Bush, U.S. Ser. No. 206,949 entitled "Oxichromic Compounds, Stabilized Oxichromic Compounds and Processes for Preparing Same," now abandoned and refiled as U.S. Ser. No. 401,327, Anderson, U.S. Ser. No. 206,925 entitled "Stabilized Oxichromic Compounds", and Stern and Machiele, U.S. Ser. No. 206,926 entitled "Stabilized Oxichromic Compounds," all filed on Dec. 10, 1971, and all incorporated herein by reference.

The above stabilized oxichromic compounds generally hydrolyze in the presence of an alkaline medium such as a pH of 9-14 and preferably above a pH of 12, in the presence of an oxidizing agent or air to provide the azomethine dye. When the azomethine dye is an indophenol, it is preferably contacted with an 'onium compound during processing to provide the 'onium indophenoxide. Generally, the stabilizing groups which are present are of low molecular weight and do not noticeably affect the diffusion rate of the developers, such as encountered in an image transfer system.

Systems can also be provided with compounds having oxichromic moieties which upon oxidation form indoanilines. Preferably, the moiety is stabilized by a hydrolyzable group attached to the reduced azomethine nitrogen atom. A typical useful compound of this type which has the general structure:

D—(OC)

as defined above is:



Compound XXVIII

Photographic systems based on these oxichromic N-dialkylindoaniline-forming compounds generally do not benefit from the 'onium salts in the image-receiving layer to control shift of light absorption and image density, etc., in the same manner as the indophenols. The compounds can also be prepared as described in Lestina and Bush, U.S. Ser. No. 206,949 entitled "Oxichromic Compounds, Stabilized Oxichromic Compounds and Processes for Preparing Same," filed on Dec. 10, 1971, now abandoned and refiled as U.S. Ser. No. 401,327.

The oxichromic compounds of this invention, and preferably the developers having the formula:

$$D—(OC)$$

as defined above, are useful in photographic systems and especially in image transfer systems. The oxichromic developers of this type are generally diffusible in an alkaline medium. In image transfer systems, the oxichromic developer is associated with a silver halide emulsion wherein the silver halide emulsion is exposed and then treated with an alkaline processing solution which permeates the layers containing the silver halide emulsion and the oxichromic developer to develop the exposed silver halide. In the areas where the silver halide emulsion is developed, the oxichromic developer is rendered relatively nondiffusing compared with the remainder of the oxichromic developer which can diffuse imagewise to an image-receiving layer wherein it can be mordanted. Upon oxidation of the oxichromic moiety, which is preferably carried out near or in the image-receiving layer, a new chromophore is formed to provide an azomethine dye.

When the OC moiety forms an indophenol, it is also desirable to incorporate an 'onium salt in the film element to provide the image dye. The 'onium salts are generally used in concentrations necessary to form an 'onium indophenoxide with all of the indophenol transferred to the receiver sheet, and are preferably sequestered from the oxichromic compound prior to processing. When the 'onium compound is immobile or ballasted and present in an image layer, it is generally utilized in concentrations of about 25 mg. to about 1000 mg/ft.^{2}, and preferably about 50 to about 500 mg./ft.^{2}, depending, of course, on the ratio of 'onium atoms to molecular weight of the compound employed. When the 'onium salt is supplied by a solution such as in the processing solution, typical useful concentrations generally range from 0.01% by weight to about 5% by weight of the 'onium compound to provide complete reaction.

The developing group D in the above oxichromic developers is generally responsible for changes in diffusibility of the oxichromic developer and, upon oxidation by reaction with exposed silver halide or an oxidized auxiliary developer, it is preferably oxidized to a relatively immobile form. In highly preferred embodiments, the group defined as D is a polyhydroxy-substituted aromatic silver halide developing function, and preferably a hydroquinone.

Black-and-white or one-color systems can be made which employ as few as one silver halide emulsion and an oxichromic developer selection which will provide the desired net color effect. Subtractive multicolor systems can also be made such as, for example, three-color systems with a blue-sensitive emulsion having associated therewith an oxichromic developer which undergoes chromogenic oxidation to produce a yellow chromophore, a green-sensitive emulsion having associated therewith an oxichromic developer which undergoes chromogenic oxidation to produce a magenta chromophore, and a red-sensitive emulsion having associated therewith an oxichromic developer which undergoes chromogenic oxidation to produce a cyan chromophore.

The oxichromic developers of this invention are especially advantageous in designing a photographic system and especially in designing an image transfer system. The oxichromic developers generally do not absorb substantial light in the visible region of the spectrum whereby they would affect the light exposure of the associated emulsion layer or a lower emulsion layer relative to the direction of exposure through the layers. Thus, the oxichromic developers can be incorporated in the silver halide emulsion layers, located in layers above the emulsion layers, etc. This feature provides considerable design freedom in making an image transfer system and a considerable improvement compared, for example, with dye-developer systems which contain a preformed dye moiety and generally require location below the emulsion layer relative to exposure direction to avoid light-absorption competition and consequent loss of speed.

Generally, the oxichromic compounds can be used in any image transfer film unit format where the respective initially diffusible oxichromic developers or the initially nondiffusible compounds are used in combination with the appropriate silver halide emulsions to achieve the desired result. Typical useful formats are disclosed in U.S. Pat. Nos. 2,543,181, 2,983,606, 3,227,550, 3,227,552, 3,415,644, 3,415,645, 3,415,646 and 3,635,707, Canadian Pat. No. 674,082, and Belgian Pat. Nos. 757,959 and 757,960, both issued Apr. 23, 1971.

Image transfer systems based on nondiffusible compounds generally contain an oxichromic moiety releasable upon redox or coupling reaction with an oxidized developing agent. Generally, the oxichromic moiety is linked to a ballasted group through a linkage which will split when the ballasted group is contacted with an oxidized silver halide developing agent to produce a diffusible dye image-providing substance of substantially lower molecular weight than the original compound, i.e., having at least a 10% and preferably at least a 30% reduction in molecular weight.

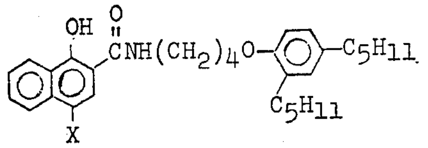
In one embodiment, the oxichromic compounds can be linked to a ballasted hydroquinone through a sulfonyl linkage, as disclosed in Gompf and Lum, U.S. Ser.

No. 160,068 filed July 6, 1971, now U.S. Pat. No. 3,698,897.

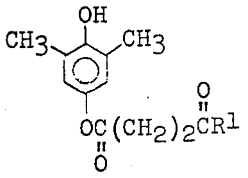
In another embodiment, the oxichromic compounds can be linked to a ballasted phenolic group through a sulfonamido linkage, as described in Fleckenstein, U.S. Ser. No. 282,795 filed Aug. 22, 1972, now abandoned and refiled as U.S. Ser. No. 351,700 on Apr. 16, 1973, said U.S. Ser. No. 282,795 being a continuation-in-part of U.S. Ser. No. 176,752 now abandoned.

In still another embodiment, the oxichromic moieties are linked to a nondiffusible coupler. The nondiffusible couplers containing releasable oxichromic indophenol moieties which are useful in image transfer systems include those ballasted compounds which are substantially nondiffusing in alkaline media and release a diffusible oxichromic moiety upon contact with an oxidized developing agent. Typical useful compounds of this type include compounds derived from the phenolic couplers and the acylacetanilide couplers such as those represented by the following formulas:

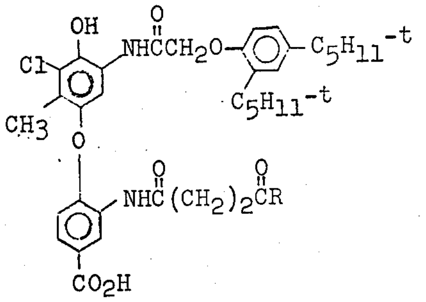
1. phenolic couplers (including naphtholic couplers)



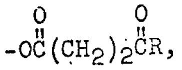
,



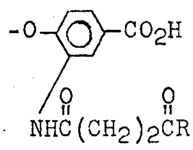
and



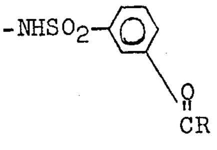
wherein X is:



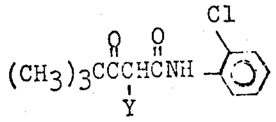
$-O\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}R,$



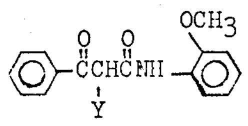
or



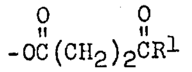
(2) acylacetanilides



and

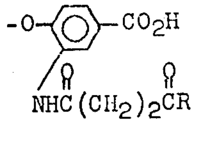


wherein Y is:

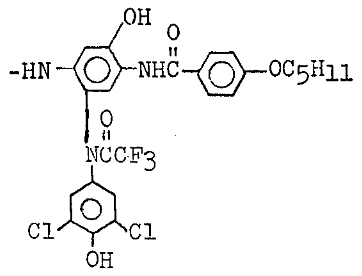


$-O\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}R^1$

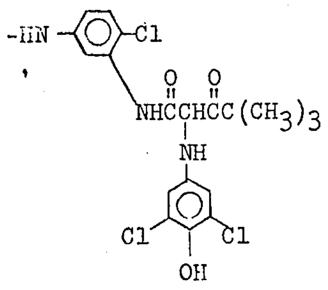
or



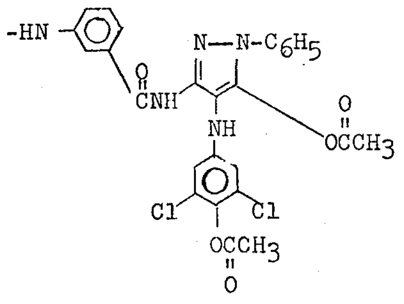
wherein R and R^1 in the above formulas can be a group as follows:



and R^1 can also be a group as follows:



or



Additional representative couplers are disclosed in U.S. Pat. Nos. 3,227,551 by Barr et al, 3,227,550 by Whitmore and 3,227,554 by Barr et al, all issued Jan. 4, 1966, and the like. The nondiffusible couplers containing oxichromic moieties can be prepared by employing the ballasted couplers in the processes of preparing oxichromic compounds which are described in Lestina and Bush, U.S. Ser. No. 206,949 entitled "Oxichromic Compounds, Stabilized Oxichromic Compounds and Processes for Preparing Same," filed on Dec. 10, 1971.

Typical useful nondiffusible compounds employed in this invention include nondiffusible couplers having the formula:

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

wherein:

1. (OC) is as defined above;
2. LINK is a connecting radical which will split when contacted with an oxidized silver halide developer, and is preferably an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical, an azoxy radical, an aminoalkyl radical as disclosed in Cressman et al, U.S. Pat. No. 3,419,390, a sulfonyloxy radical as disclosed in Porter, U.S. Pat. No. 3,415,652, an acyloxy radical as disclosed in Loria, U.S. Pat. No. 3,311,476, and an imido radical as dis-

closed in Loria, U.S. Pat. No. 3,458,315, and also could be a sulfonyl radical or a sulfonamido radical;

3. COUP is a coupler radical such as a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, COUP being substituted in the coupling position with LINK;

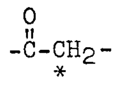
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render such coupler nondiffusible during development in an alkaline processing composition; and

5. *n* is generally an integer of 1, provided that when LINK is an alkylidene radical *n* can be an integer of 1 or 2.

Acidic solubilizing radicals are generally attached to the diffusible moiety of the compounds described, which can be solubilizing radicals which, when attached to the dye-providing moiety, render the dyes diffusible in alkaline processing compositions. Typical of such radicals are carboxylic, sulfonic, ionizable sulfonamide and hydroxy-substituted groups that lend to dyes negative charges.

The nature of the ballast groups in the diffusible dye-producing compounds described above (BALL-) is not critical as long as they confer nondiffusibility to the coupler compounds. Typical ballast groups include long-chain alkyl radicals linked directly or indirectly to the coupler molecules, as well as aromatic radicals of the benzene and naphthalene series, etc., linked directly or indirectly to the coupler molecules by a splittable linkage, or by a removable or irremovable but otherwise nonfunctional linkage depending upon the nature of the coupler compound. Generally, useful ballast groups have at least 8 carbon atoms.

With regard to the above-described coupler radicals (COUP-), the "coupling position" is well-known to those skilled in the photographic art. The 5-pyrazolone coupler radicals couple at the carbon atom in the 4-position, the phenolic coupler radicals, including α-naphthols, couple at the carbon atom in the 4-position, and the open-chain ketomethylene coupler radicals couple to the carbon atom forming the methylene moiety (e.g.,



$$-\overset{O}{\overset{\|}{C}}-\underset{*}{CH_2}-$$

* denoting the coupling position). Pyrazolotriazole couplers and their coupling position are described, for example, in U.S. Pat. No. 3,061,432 and U.S. Ser. No. 778,329 of Bailey et al. filed Nov. 22, 1968. Further structural definitions on couplers of this type are given in U.S. Pat. No. 3,620,747 issued Nov. 16, 1971, which is incorporated herein by reference.

When couplers having the formula:

$$OC—LINK—(COUP\text{-}BALL)_n$$

as described above are reacted with an oxidized color developing agent, the connecting radical (LINK) is split and a diffusible compound is released which is a dye image-providing material which diffuses imagewise to a reception layer. Diffusibility can be imparted to the dye image-providing material by solubilizing groups attached thereto. The ballasted portion of the coupler remains immobile. In this type of system, the color is determined by the chromophore formed during processing.

In using the above couplers in the invention, the production of diffusible dye image-providing material is a function of the reduction of developable silver halide images which may involve direct or reversal development of the silver halide emulsions with an aromatic primary amine developing agent. It the silver halide emulsion employed in a direct-positive silver halide emulsion, such as an internal-image emulsion or a solarizing emulsion, which is developable in unexposed areas, a positive image can be obtained in the receiver portion of the film unit. In this embodiment, the nondiffusible coupler can be located in the silver halide emulsion itself. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the exposed layers of photosensitive silver halide emulsion. The developing agent becomes oxidized imagewise, corresponding to the unexposed areas of the direct-positive silver halide emulsion layers. The oxidized developing agent then reacts with the nondiffusible coupler present in each silver halide emulsion layer to form imagewise distributions of diffusible image-providing materials 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 material diffuses to the image-receiving layer and upon oxidation, and in some instances upon contact with an 'onium compound, the image dye is produced. After being contacted by the alkaline processing composition, a pH-lowering layer in the film unit, if one is present, lowers the pH of the film unit to stabilize it. Further details of nondiffusing couplers and coupler-release chemistry are found in U.S. Pat. Nos. 3,227,550 and 3,227,552, which are incorporated herein by reference.

Another embodiment of the invention employing the nondiffusible couplers described above to produce a diffusible dye image-providing substance is to employ them in combination with development inhibitor-releasing couplers as described in U.S. Pat. No. 3,227,551. In such an embodiment, the photosensitive portion of the photosensitive element would comprise at least two color-forming units in layers sensitive to different regions of the visible spectrum, separated by a barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans, each of the color-forming units comprising:

1. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by a color-developing agent to substantial density without exposure to light, the metal salt having contiguous thereto the nondiffusible coupler capable of reacting with an oxidized color-developing agent to form a diffusible dye image-providing substance and

2. a photosensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with an oxidized color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to the adjacent developable emulsion layer to inhibit development therein.

The developing agent is preferably an aromatic primary amine and is generally present in the alkaline processing composition, and the developable emulsion is preferably an emulsion of a hydrophilic colloid, silver thiocyanate and physical development nuclei that can be developed to substantial density without exposure to light. The developable emulsion can also be made from a metal salt which is made spontaneously developable by incorporating in the emulsion a wide variety of well-known physical development nuclei as disclosed in the above-mentioned U.S. Pat. No. 3,227,551, column 6, lines 63–75, and column 7, lines 1–10. Another method that can be utilized to make the water-insoluble salts spontaneously developable is by prefogging the emulsion with light or with chemical reducing agents such as alkali metal borohydrides and the like in accordance with well-known photographic fogging techniques.

In another embodiment of the invention, the nondiffusible couplers described above are used in combination with physical development nuclei in a nuclei layer associated with each photosensitive silver halide emulsion layer to produce a diffusible dye image-providing material. The film unit contains a silver halide solvent, preferably in a rupturable container with the alkaline processing composition, and each photosensitive silver halide emulsion layer contains an immobilizing coupler e.g., a coupler with a ballast group, which is capable of reacting with an oxidized color developing agent to form an immobile product. Each photosensitive silver halide emulsion layer and its associated nuclei layer are separated from the other silver halide emulsions and their associated nuclei layers in the film unit by means of an alkaline solution-permeable barrier layer for retaining silver complexes. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the latent image contained in each photosensitive silver halide emulsion layer. The color developing agent present in the film unit develops each of the exposed silver halide emulsion layers, thus causing the color developing agent to become oxidized imagewise. The oxidized developing agent then reacts with the immobilizing coupler present in each said photosensitive silver halide emulsion layer to form an immobile product. The remaining silver halide in each silver halide emulsion layer corresponding to unexposed and thus undeveloped areas forms a soluble silver ion complex with the silver halide solvent present in or activated by the processing composition and migrates to each associated nuclei layer. The transferred silver complex is reduced or physically developed in the nuclei layer, thus causing the developing agent to become oxidized. The oxidized developing agent then reacts with the nondiffusible coupler present in each nuclei layer to release imagewise distributions, respectively, of a diffusible cyan-forming oxichromic compound, a magenta-forming oxichromic compound and a yellow-forming oxichromic compound as a function of the imagewise exposure of each said silver halide emulsion layer. At least a portion of said imagewise distributions of diffusible oxichromic compounds then diffuses to the image-receiving layer which, upon oxidation and in some instances upon contact with an 'onium compound, provides positive dye images. After being contacted by the alkaline processing composition, a pH-lowering layer in the film unit, if one is present, lowers the pH of the film unit to stabilize it.

In the above-described embodiment, the physical development nuclei can be any of those well-known to those in the art such as colloidal metals, e.g., colloidal silver, gold, platinum, palladium, colloidal metal sulfides, e.g., colloidal silver sulfide, zinc sulfide, etc. Materials which form physical development nuclei may also be used, such as reducing agents and labile sulfur compounds. The nuclei layer can also be split into two layers, one on each side of the photosensitive silver halide emulsion layer, if desired. The silver halide solvent employed can be any of those well-known to those skilled in the art, such as alkali metal and ammonium thiosulfates and thiocyanates, e.g., sodium thiosulfate, ammonium thiosulfate, ammonium thiocyanate, potassium thiocyanate, etc., and may be incorporated in a separate layer, if desired. Spacer layers comprising gelatin are preferably employed between the nuclei layers and the photosensitive silver halide emulsion layers to prevent undesirable mixing of the two layers upon coating. The spacer layers may also contain nuclei and a nondiffusible coupler capable of reacting with oxidized color developing agent to form an immobile product in order to increase it efficiency. Other details concerning this type of photographic chemistry are found in British Pat. No. 904,364, page 19, lines 1–41.

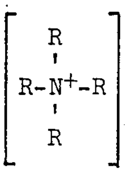
In the above-described embodiments employing nondiffusible couplers, interlayers are generally employed between the various photosensitive color-forming units to scavenge the oxidized developing agent and prevent it from forming an unwanted dye in another color-forming unit. Such interlayers would generally comprise a hydrophilic polymer such as gelatin and an immobilizing coupler, as described above, which is capable of reacting with an oxidized color developing agent to form an immobile product. Such interlayers may also scavenge other materials such as soluble silver ion complexes or mercaptans in the described systems to prevent such materials from contaminating other color-forming units. A developer scavenging interlayer may also be employed in the above-described embodiments adjacent the light-reflective layer to prevent excess color developing agent from staining the image-receiving layer. Such a layer can comprise, for example, a nondiffusible coupler capable of reacting with an oxidized color developing agent to form an immobile product and a silver halide emulsion, preferably one which is developable without exposure.

Generally, the dye image-providing substances referred to above, which include the oxichromic developers, the nondiffusible couplers and the like, can be incorporated in the photographic elements in sufficient quantities to provide the desired image dye density after processing as known in the art for dye image-providing materials. The concentrations will vary, of course, depending on the type of compound employed, the film unit structure and the like.

In accordance with this invention, when indoarylene compounds such as indophenols are formed in the process, they are preferably contacted with 'onium compounds to form 'onium indophenoxides. The 'onium compounds can either be soluble compounds which can be added by contacting the indophenol with a solution of the 'onium compound or be high-molecular-weight compounds which are relatively insoluble in water and can be placed in at least one layer of the photograpahic element, such as in the mordant layer where the indophenol produces the 'onium indophenoxide image dye.

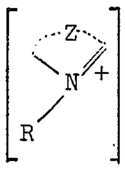
In one embodiment, especially useful dye images have been obtained through the combination of indophenols and quaternary ammonium compounds. As is known, quaternary ammonium compounds are organic compounds containing a nitrogen atom having a net positive charge. Generally, they can be considered as derivatives of ammonium compounds wherein the four valences usually occupied by the hydrogen atoms are occupied by organic radicals. Generally, the organic radicals are joined directly to the nitrogen through a single or double carbon-to-nitrogen bond. The term "quaternary ammonium," as used herein, is intended to cover compounds wherein said nitrogen is one of the nuclear atoms in a heterocyclic ring, as well as those wherein each of the four valences is attached to separate organic radicals, e.g., tetraalkyl quaternary ammonium compounds. As illustrations of quaternary ammonium compounds, mention may be made of those represented by the following formulae:

(1)



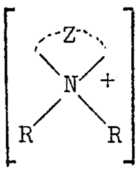
$$\left[R_4N^+\right] Y^-,$$

(2)



Y^- and

(3)



Y^-

wherein each R is an organic radical; Y is an anion, e.g., hydroxy, bromide, chloride, toluenesulfonate, etc.; and Z represents the atoms necessary to complete a heterocyclic ring. As examples of compounds with Formulae 1, 2 and 3, mention may be made of tetraethylammonium bromide, N-ethylpyridinium bromide, N,N-diethylpiperidinium bromide, ethylene-bis-pyridinium bromide, 1-ethylpyridinium bromide, 1-phenethyl-3-picolinium bromide, tetraalkylammonium salts, cetytrimethylammonium bromide, polyalkylene oxide bis-quaternary ammonium salts such as polyethylene oxide bis-pyridinium perchlorate, the heterocyclic quaternary ammonium salts mentioned which form the methylene bases including 3-methyl-2-ethylisoquinolinium bromide, 3-methylisoquinolinium methyl-p-toluenesulfonate, 1-ethyl-2-methyl-3-phenethylbenzimidazolium bromide, 5,6-dichloro-1-ethyl-2-methyl-3-(3-sulfobutyl)benzimidazolium betaine and the pyridinium salts below.

Other useful 'onium compounds include tertiary sulfonium and quaternary phosphonium compounds which are represented by the formulae:

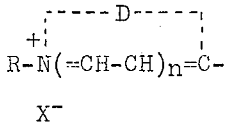
(4) $(R)_3S^+X^-$ and (5) $(R)_4P^+X^-$

wherein each R is an organic radical, e.g., alkyl, aralkyl, aryl, etc., groups; and X is an anion, e.g., hydroxy, bromide, chloride, toluenesulfonate, etc. As examples of tertiary sulfonium and quaternary phosphonium compounds, mention may be made of lauryldimethylsulfonium p-toluenesulfonate, nonyldimethylsulfonium p-toluenesulfonate and octyldimethylsulfonium p-toluenesulfonate, butyldimethylsulfonium bromide, triethylsulfonium bromide, tetraethylphosphonium bromide, dimethylsulfonium p-toluenesulfonate, dodecyldimethylsulfonium p-toluenesulfonate, decyldimethylsulfonium p-toluenesulfonate and ethylene-bis-oxymethyltriethylphosphonium bromide.

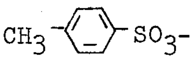
The 'onium compounds may be used as the hydroxide or as the salt. When the 'onium compounds are used as the salt, the anion may be a derivative of any acid. However, it should be noted that when the anion is iodide, such iodide may have deleterious effects on the emulsion and suitable precautions should be taken if it is to be in contact with the emulsion before development is complete. Especially good results are obtained when the 'onium compounds employed are bromides.

Useful heterocyclic quaternary ammonium compounds which form the methylene bases diffusible in alkaline solution have the general formula:

(6)



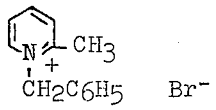
wherein D represents the nonmetallic atoms necessary to complete the heterocyclic nucleus of the quaternary ammonium compound containing 1 or more of the reactive methyl groups —CH_2R' in one or more of the nuclear positions, the other nuclear positions being substituted or not, such as quaternary salts of the pyridine, quinoline, benzoquinoline, benzoxazole, benzoselenazole, thiazole, benzothiazole, naphthothiazole, benzimidazole, isoquinoline series, etc.; *n* is 0 or 1; R is an alkyl group, an aryl or aralkyl group of the benzene series, or substituted alkyl, aryl or aralkyl groups of the benzene series, the alkyl chains preferably being lower alkyl of from 1 to 4 carbon atoms; R' is a hydrogen atom or one of the groups represented by R; and X represents OH— of an acid anion such as Br—, CH_3SO_4— or



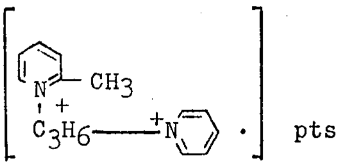
One or more of these quaternary ammonium compounds can be used alone or in combination with the 'onium compounds having the Formulae 1, 2, 3, 4 and 5 above, and are advantageously employed in either the processing solution, the photographic element, or both.

Typical 'onium salts which are useful in the invention which form diffusible methylene bases are as follows:

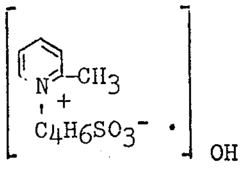
1-benzyl-2-picolinium bromide



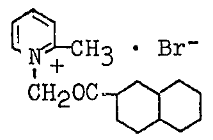
1-(3-bromopropyl)-2-picolinium p-toluenesulfonate
1-phenethyl-2-picolinium bromide
1-γ-phenylpropyl-2-picolinium bromide
2,4-dimethyl-1-phenethylpyridinium bromide
2,6-dimethyl-1-phenethylpyridinium bromide
5-ethyl-2-methyl-1-phenethylpyridinium bromide
2-ethyl-1-phenethylpyridinium bromide
1-[3-(N-pyridinium bromide)propyl]-2-picolinium p-toluenesulfonate



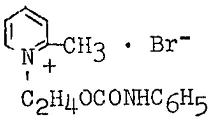
anhydro-1-(4-sulfobutyl)-2-picolinium hydroxide



α-picoline-β-naphthoylmethyl bromide



1-β-phenylcarbamoyloxyethyl-2-picolinium bromide



1-methyl-2-picolinium p-toluenesulfonate
1-phenethyl-2,4,6-trimethylpyridinium bromide
1-phenethyl-4-n-propylpyridinium bromide
4-γ-hydroxypropyl-1-phenethylpyridinium bromide and 1-n-heptyl-2-picolinium bromide

In highly preferred embodiments of the invention, the image dye is mordanted in a polymeric material such as a polymer with 'onium groups thereon. Typical useful mordants of this type are vinylpyridinium compounds of the type disclosed in U.S. Pat. No. 2,484,430 issued Nov. 10, 1949; polymers containing quaternary ammonium groups such as disclosed in U.S. Ser. Nos. 734,873 by Cohen et al filed June 6, 1968 Pat. No. 3,625,694 issued Dec. 7, 1971, 100,487 by Cohen et al filed Dec. 21, 1970, now U.S. Pat. No. 3,758,445 issued Sept. 11, 1973, 100,491 by Cohen et al filed Dec. 21, 1970 Pat. No. 3,709,690 issued Jan. 9, 1973, and 709,793 by Cohen et al filed Mar. 1, 1968, now U.S. Pat. No. 3,639,357 issued Feb. 1, 1972 and U.S. Pat. No. 3,488,706 by Cohen et al issued Jan. 6, 1970, and 3,557,006 by Cohen et al issued Jan. 19, 1970; and the like.

In another preferred embodiment, the mordant is an 'onium coacervate mordant such as disclosed in Bush, U.S. Pat. No. 3,271,147 issued Sept. 6, 1966.

In another embodiment, the photographic elements of this invention contain an image-receiving layer which comprises a polyvinylpyridine mordant. Certain oxichromic compounds of this invention undergo chromogenic oxidation and are mordanted on the polyvinylpyridine to provide very good image dye characteristics.

In the drawings, FIGS. **1–4** are graphs representing the absorption characteristics of the oxichromic compounds of Examples 1, 2, 9 and 22.

In FIGS. **5–7**, a preferred film unit of the invention is described with the various elements magnified for purposes of illustration only wherein like numbers appearing in the various figures refer to like components.

In FIG. **5**, rupturable container **11** is positioned transverse a leading edge of the photosensitive laminate and is held in place by binding means **30**, which can be a pressure-sensitive tape or the like which encloses that edge of the laminate. The other edges of the photosensitive laminate are sealed together, either directly or with a spacer member, to prevent leakage of processing solution during and after photographic processing when rupturable container **11** is broken open by pressure-applying members **36** to discharge its contents into the photosensitive laminate.

In FIG. **6**, a film unit **10** comprises rupturable container **11** containing, prior to passing between pressure-applying members **36**, an alkaline processing composition **12** containing an opacifying agent and a photosensitive laminate comprising top transparent sheet **26** coated with polymeric acid layer **25** and polymeric timing layer **24** and a photosensitive element comprising a transparent support layer **15** coated with an image-receiving layer **16** associated with an oxidizing agent, an opaque reflecting layer **17**, preferably an actinic radiation-opaque layer **18** which can also be a scavenger layer, a red-sensitive silver halide emulsion layer **19** associated with a cyan dye image-providing material, interlayer **20**, a green-sensitive silver halide emulsion layer **21** associated with a magenta dye image-providing material, interlayer **22**, and a blue-sensitive silver halide emulsion layer **23** associated with a yellow dye image-providing material. Exposure of the film unit takes place through the top transparent sheet **26** which is preferably an actinic radiation-transmissive flexible sheet material.

In FIG. **7**, film unit **10** has been passed between pressure-applying members **36** such as would be found in a camera, thus causing rupturable container **11** to collapse and discharge the alkaline processing composition **12** containing an opacifying agent between the polymeric timing layer **24** and the blue-sensitive silver halide emulsion layer **23**. After development and image transfer has taken place, a positive, right-leading image may be viewed through transparent support **15**.

The structural integrity of the photosensitive laminate can be maintained, at least in part, by the adhesive characteristics between the various layers of the laminate. However, the adhesion exhibited at the interface between the polymeric timing layer **24** of top transparent sheet **26** and underlying layer **23** is less than the adhesion at the remaining interfaces of the laminate in order to facilitate distribution of processing composition **12** between these two layers.

The film unit of our invention may be constructed by assembling the various parts in an atmosphere maintained at a pressure lower than atmospheric pressure and by sealing the transparent sheet to the photosensitive element along their edges in order to prevent the admission of air between them. The exclusion of air between the transparent sheet and the photosensitive element is desirable in order to prevent air bubbles from being entrained in the processing composition which would form discontinuities in the positive image. Details of this method of assembly and other methods for assuring a uniform distribution of processing composition between two sheets are described in Belgian Pat. No. 711,897.

The film unit of our invention can also contain a liquid trap at the opposite end from which processing composition is introduced in order to trap any excess processing composition and keep it from being expelled from the film unit. The liquid trap may also function to let air escape, if any is present. Such liquid traps are disclosed, for example, in Belgian Pat. No. 711,899.

The film unit of our invention may also be processed in the manner described in Belgian Pat. No. 711,898 wherein two sets of pressure rollers are used in order to expel any air between the transparent sheet and the photosensitive element and also to facilitate an even distribution of processing composition between said sheet and element. The transparent sheet in our film unit may also be fluted along the length of the side edges, similar to the technique described in Belgian Pat. No. 711,898, in order to assist in distributing the processing composition evenly between the transparent sheet and the photosensitive element.

If it is desired to have residual water in the film unit leave the system after processing, this may be accomplished by incorporating into the film unit a desiccating layer to absorb water or by providing access to the atmosphere in order to let the water evaporate, e.g., by employing a water-permeable transparent sheet or a water-permeable film support for the photosensitive element or by allowing water to evaporate through the liquid traps in the film unit as described above, etc.

Rupturable container **11** can be of the type disclosed in U.S. Pat. Nos. 2,543,181, 2,634,886, 2,653,732, 2,723,051, 3,056,492, 3,056,491 and 3,152,515. In general, such containers comprise a rectangular sheet of fluid- and air-impervious material folded longitudinally upon itself to form two walls which are sealed to one another along their longitudinal and end margins to form a cavity in which processing composition **12** containing an opacifying agent is contained (see FIG. **6**). The longitudinal marginal seal **35** is made weaker than the end margin seals so as to become unsealed in response to the hydraulic pressure generated within the fluid contents **12** of the container by the application of a compressive force to the outside walls of the container.

As illustrated in FIGS. **5** and **6**, container **11** is fixedly positioned and extends transverse a leading edge of the photosensitive laminate so that a compressive force applied to said container will effect a unidirectional discharge of the container's contents between the polymeric timing layer **24** of top transparent sheet **26** and underlying layer **23**. In FIG. **6**, the weak longitudinal marginal seal **35** is directed toward the interface between layers **23** and **24** to facilitate this operation.

In the performance of a multicolor diffusion transfer process employing film unit **10**, the unit is exposed to radiation incident on the photosensitive laminate's upper surface through transparent sheet **26**, as illustrated in FIG. **6**. Subsequent to exposure, the film unit **10** is processed by passing it between pressure-applying members **36** in order to apply compressive pressure to frangible container **11** and to effect rupture of longitudinal seal **35** and distribution of alkaline processing composition **12** containing an opacifying agent between layers **24** and **23** of film unit **10**. The alkaline processing composition permeates the silver halide emulsion layers **23, 21** and **19** to initiate imagewise development of the silver halide. Diffusible yellow, magenta and cyan dye image-providing materials are formed from material associated with the silver halide emulsion in layers **23, 21** and **19** as a function of the imagewise exposure of their associated emulsions. At least part of the imagewise distributions of mobile yellow-, magenta- and cyan-forming materials transfer, by diffusion, to the image-receiving layer **16** to provide a positive dye image therein upon chromogenic oxidation. This positive, right-reading image can then be viewed through transparent support layer **15** on the opaque reflecting layer **17** background. Since the receiving layer does not have to be stripped away from the negative portion of the film unit, the composite structure can be maintained intact subsequent to said processing.

In accordance with the invention, oxichromic compounds which are colorless permit exposure through the required side and still retain effective contact with the silver halide emulsion to render the dye image-providing material nondiffusing in the developed areas, thus avoiding severe color contamination, especially with the oxichromic developers. The oxichromic developers can be incorporated in the emulsion layer or positioned between the emulsion layer and the exposure source without substantial competitive light absorption, so that a highspeed photographic system with this format based on negative emulsions and diffusible dye image-providing substances can now be made.

Generally, oxidation of the oxichromic compounds which diffuse to the image-receiving layer can be achieved by using a porous support next to the mordant layer wherein air can permeate the support to provide chromogenic oxidation. In preferred embodiments, the oxichromic compounds are stabilized; therefore, oxidation will not occur until the reaction has first been base catalyzed. In one embodiment, an oxidant is provided next to the mordant or image-receiving layer. When the oxidant is a mobile compound, it is preferably retained in a layer beneath the mordant by a timing layer to prevent premature oxidation. Suitable timing layers are more fully described hereinafter. However, when the oxidant is an immobile compound, it can be incorporated in the mordant layer wherein oxidation will occur upon mordanting the image-providing material. Typical useful oxidants include inorganic, organic, monomeric, polymeric, mobile or immobile compounds. Specific useful types of oxidants include borates, persulfates, ferricyanides, periodates, perchlorates, triiodides, permanganates, dichromates, manganese dioxide, silver halides, benzoquinones, naphthoquinones, disulfides, nitrogen oxides, heavy metal oxidants, heavy metal oxidant chelates, N-bromosuccinimides, nitroso compounds, ether peroxides, and the like. The oxidant can also be present in a separate container means which is ruptured to effect contact of the oxidant with an oxichromic compound.

In one highly preferred embodiment, the oxichromic compounds of this invention are especially useful in image transfer systems where the image-receiving layer is separated from the silver halide emulsion layers after processing and transfer of the image dye-providing material. In formats of this type, air contact after separation of the image-receiving layer from the silver halide emulsion layers can serve to oxidize the oxichromic developers to form the image dyes. Typical image transfer formats of this type are disclosed in U.S. Pat. Nos. 2,543,181 issued Feb. 27, 1951, 3,266,894 issued Apr. 16, 1966, 3,309,201 issued Mar. 14, 1967, 2,661,293 issued Dec. 1, 1953, 2,698,244 issued Dec. 28, 1954, and the like.

Generally, the oxichromic developers of this invention can be used to obtain highly improved image transfer systems in formats designed for use with dye image-providing materials that are soluble in alkaline processing compositions (i.e., initially diffusible) such as, for example, diffusible color couplers as described in U.S. Pat. No. 2,661,293, diffusible dyes such as described in U.S. Pat. No. 2,774,668, diffusible developing agents such as mentioned in U.S. Pat. No. 2,992,105, and the like. The oxichromic developers are very useful in image transfer systems of this type since they are colorless and can be incorporated directly in the silver halide emulsion layer providing intimate association with the silver halide emulsion upon permeation with the alkaline processing solution, thus providing the option of a six-layer structure instead of a nine-layer structure used where the image dyes are present during exposure. We have found that oxichromic developers are very efficient developers by themselves when incorporated in the emulsion and do not require an auxiliary developer to obtain fast silver halide development and immobilization of the oxichromic compound. The auxiliary black-and-white developer which was generally essential with other initially diffusible compounds, such as dye developers, to obtain rapid redox reaction and immobilization of the dye-providing compound, as mentioned in U.S. Pat. Nos. 3,192,044 and 2,983,606, is not essential to image transfer systems containing the oxichromic developers of this invention.

We have also found that the oxichromic developers of this invention can be coated in a monopack three-color integral negative structure using the same binder for all layers (i.e., silver halide emulsion layers and interlayers) to provide good transfer images without substantial interimage contamination. Thus, means to control migration of the dye image-providing material from its initial layer unit until after development of adjacent layers are not required.

In one preferred embodiment, we have found that certain auxiliary developers can be used in an image transfer film unit containing oxichromic developers to reduce interlayer contamination. Since development of the silver halide layers occurs very rapidly with the associated oxichromic developer, an auxiliary developer can be positioned in the film unit whereby it will contact the silver halide layers only after substantial development has taken place in the respective silver halide layers. Thus, all remaining developable silver halide can be developed before substantial diffusion into this layer of an oxichromic developer from an adjacent layer occurs. The auxiliary developer can be located in the image-receiving layer where it will be delayed in migration to the silver halide layers, it can be located in or behind timing layers which release it at a predetermined time, it can be located in interlayers, or it can be a slowly diffusing auxiliary developer located in the rupturable container used for the aqueous processing composition. In one highly preferred embodiment, a slowly diffusing auxiliary developer is used which is a high-molecular-weight polycyclic compound, preferably having at least three bridged or fused rings such as, for example, 5,6,7,8-tetrahydro-5,8-methano-1,4-naphthalene diol and the like. The slowly diffusing auxiliary developing agents of this type are preferably located in the processing pod along with the alkaline processing composition. Other useful developing agents of this type or tautomers thereof are disclosed in U.S. Pat. No. 3,287,129 issued Nov. 22, 1956. It is also contemplated that auxiliary developing agents having slowly hydrolyzing groups such as acyl groups, acyloxy groups and the like could be used to delay the reaction of the auxiliary developing agent in the silver halide layers.

In certain embodiments, the alkaline processing composition or photographic element can also contain an auxiliary or accelerating developing agent other than described next above which does not contain the structure D—(OC) as defined above. Typical useful auxiliary developing agents are p-methylaminophenol, 2,4-diaminophenol, p-benzylaminophenol, hydroquinone, toluhydroquinone, phenylhydroquinone, 4-methylphenylhydroquinone, 1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl pyrazolidone, etc. A plurality of auxiliary or accelerating developing agents such as those disclosed in U.S. Pat. No. 3,039,869 can also be employed. Such auxiliary or accelerating developing agents can be employed in the liquid processing composition or may be contained, at least in part, in any layer or layers of the film unit such as the silver halide emulsion layers, the dye image-providing material layers, interlayers, image-receiving layer, etc. In certain preferred embodiments, a slowly diffusing auxiliary developer can be used, especially when located in the rupturable container.

In a color film unit according to the invention, each silver halide emulsion layer containing a dye image-providing material or having the dye image-providing material present in a contiguous layer may be separated from the other silver halide emulsion layers in the negative portion of the film unit by materials in addition to those described above, including gelatin, calcium alginate, or any of those disclosed in U.S. Pat. No. 3,384,483, polymeric materials such as polyvinylamides as disclosed in U.S. Pat. No. 3,421,892, or any of those disclosed in French Pat. No. 2,028,236 or U.S. Pat. Nos. 2,992,104, 3,043,692, 3,044,873, 3,061,428, 3,069,263, 3,069,264, 3,121,011 and 3,427,158.

Generally speaking, except where noted otherwise, the silver halide emulsion layers in the invention comprise photosensitive silver halide dispersed in gelatin and are about 0.6 to 6 microns in thickness; the dye image-providing materials are dispersed in an aqueous alkaline solution-permeable polymeric binder such as gelatin, as a separate layer about 1 to 7 microns in thickness; and the alkaline solution-permeable polymeric interlayers, e.g., gelatin, are about 1 to 5 microns in thickness. Of course, these thicknesses are approximate only and can be modified according to the product desired. In addition to gelatin, other suitable hydrophilic materials include both naturally occurring substances such as proteins, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water-soluble polyvinyl compound 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 combinaton 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 U.S. Pat. Nos. 3,142,568 by Nottorf issued July 28, 1964, 3,193,386 by White issued July 6, 1965, 3,062,674 by Houch et al issued Nov. 6, 1962, 3,220,844 by Houck et al issued Nov. 30, 1965, 3,287,289 by Ream et al. issued Nov. 22, 1966, and 3,411,911 by Dykstra issued Nov. 19, 1968. Particularly effective are 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, and those having recurring sulfobetaine units as described in Dykstra, Canadian Pat. No. 774,054.

Any material can be employed as the image-receiving layer in this invention as long as the desired function of mordanting or otherwise fixing the dye images will be obtained. The particular material chosen will, of course, depend upon the dye image to be mordanted as mentioned hereinbefore.

use of a pH-lowering layer in the film unit of the invention will usually increase the stability of the transferred image. Generally, the pH-lowering layer will effect a reduction in the pH of the image layer from about 13 or 14 to at least 11 and preferably 5–8 within a short time after imbibition. For example, polymeric acids as disclosed in U.S. Pat. Nos. 3,362,819 issued Jan. 9, 1968, 2,584,030 issued Jan. 29, 1952, or 2,548,575 issued Apr. 10, 1951, or Belgian Pat. No. 603,747 issued May 31, 1961, p. 47, may be employed. Such polymeric acids reduce the pH of the film unit after development to terminate development and substantially reduce further dye transfer and thus stabilize the dye image. Such polymeric acids comprise polymers containing acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium or potassium, or with organic bases, particularly quaternary ammonium bases, such as tetramethy ammonium hydroxide. The polymers can also contain potentially acid-yielding groups such as anhydrides or lactones or other groups which are capable or reacting with bases to capture and retain them. Generally, the most useful polymeric acids contain free carboxyl groups, being insoluble in water in the free acid form and which form water-soluble sodium and/or potassium salts. Examples of such polymeric acids include dibasic acid half-ester derivatives of cellulose, which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen gluturate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with orthosulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid, acetals of polyvinyl alcohol with carboxy or sulfo-substituted aldehydes, e.g., o-, m- or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methylvinyl ether/maleice anhydride copolymers; etc. In addition, solid monomeric acid materials could also be used such as palmitic acid, oxalic acid, sebacic acid, hydrocinnamic acid, metanilic acid, paratoluenesulfonic acid and benzenedisulfonic acid. Other suitable materials are disclosed in U.S. Pat. Nos. 3,422,075 and 2,635,048.

The pH-lowering layer is usually about 0.3 to about 1.5 mils in thickness and can be located in the receiver portion of the film unit between the support and the image-receiving layer, on the cover sheet as shown in FIG. **6**, or anywhere within the film unit as long as the desired function is obtained.

An inert timing or spacer layer coated over the pH-lowering layer may also be used to "time" or control the pH reduction of the film unit as a function of the rate at which the alkali diffuses through the inert spacer layer. Timing layers can also be used effectively to isolate oxidizing materials in a layer adjacent the image-receiving layer wherein oxidant will be released after alkali breakdown of the timing layer. Examples of such timing layers include gelatin, polyvinyl alcohol or any of those disclosed in U.S. Pat. No. 3,455,686. The timing layer is also effective in evening out the various reaction rates over a wide range of temperatures, e.g., premature pH reduction is prevented when imbibition is effected at temperatures above room temperature, for example, at 95° to 100° F. The timing layer is usually about 0.1 to about 0.7 mil in thicknes. Especially good results are obtained when the timing layer comprises a hydrolyzable polymer or a mixture of such polymers which are slowly hydrolyzed by the processing composition. Examples of such hydrolyzable polymers include polyvinyl acetate, polyamides, cellulose esters, etc.

The alkaline processing composition employed in this invention is the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 12, and preferably containing a developing agent as described previously. The solution also preferably contains a viscosity-increasing compound such as a high-molecular-weight polymer, e.g., a water-soluble ether inert to alkaline solutions such as hydroxyethyl cellulose or alkali metal salts of carboxymethyl cellulose such as sodium carboxymethyl cellulose. A concentration of viscosity-increasing compound of about 1 to about 5% by weight of the processing solution is preferred which will impart thereto a viscosity of about 100 cps. to about 200,000 cps. If desired, an adhesive may be added to the processing composition to increase further the adhesion of the transparent sheet to the photosensitive element after processing such as in liquid formats.

The alkaline processing composition employed in this invention can also contain a desensitizing agent such as methylene blue, nitro-substituted heterocyclic compounds, 4,4′-bipyridinium salts, etc., to insure that the photosensitive element is not further exposed after it is removed from the camera for processing.

While the alkaline processing composition used in this invention can be employed in a rupturable container, as described previously, to facilitate conveniently the introduction of processing composition into the film unit, other means of discharging processing composition within 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, as described in Harvey, U.S. Pat. No. 3,352,674 issued Nov. 14, 1967.

In certain embodiments of our invention, and especially with integral format film units, an opacifying agent can be employed in the processing composition in our invention. Examples of opacifying agents include carbon black, barium sulfate, zinc oxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, titanium dioxide, organic dyes such as the nigrosines, or mixtures thereof in widely varying amounts depending upon the degree of opacity desired. In general, the concentration of opacifying agent should be sufficient to prevent further exposure of the film unit's silver halide emulsion or emulsions by ambient actinic radiation through the layer of processing composition, either by direct exposure through a support or by light piping from the edge of the element. For example, carbon black or titanium dioxide will generally provide sufficient opacity when they are present in the processing solution in an amount of from about 5 to 40% by weight. After the processing solution and opacifying agent have been distributed into the film unit, processing may take place out of the camera in the presence of actinic radiation in view of the fact that the silver halide emulsion or emulsions of the laminate are appropriately protected by incident radiation, at one major surface by the opaque processing composition and at the remaining major surface by the alkaline solution-permeable opaque layer. Opaque binding tapes can also be used to prevent edge leakage of actinic radiation incident on the silver halide emulsion.

When titanium dioxide or other white pigments are employed as the opacifying agent in the processing composition in our invention, it may also be desirable to employ in cooperative relationship therewith a pH-sensitive opacifying dye such as a phthalein dye. Such dyes are light-absorbing or colored at the pH at which image formation is effected and colorless or not light-absorbing at a lower pH. Other details concerning these opacifying dyes are described in French Pat. No. 2,026,927.

The alkaline solution-permeable, substantially opaque, light-reflective layer in the integral negative receiver film units of our invention can generally comprise any opacifier dispersed in a binder as long as it has the desired properties. Particularly desirable are white light-reflective layers since they would be esthetically pleasing backgrounds on which to view a transferred dye image and would also possess the optical properties desired for reflection of incident radiation. Suitable opacifying agents include titanium dioxide, barium sulfate, zinc oxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, or mixtures thereof in widely varying amounts depending upon the degree of opacity desired. The opacifying agents may be dispersed in any binder such as an alkaline solution-permeable polymeric matrix such as, for example, gelatin, polyvinyl alcohol, and the like. Brightening agents such as the stilbenes, coumarins, triazines and oxazoles can also be added to the light-reflective layer, if desired. When it is desired to increase the opacifying capacity of the light-reflective layer, dark-colored opacifying agents may be added to it, e.g., carbon black, nigrosine dyes, etc. Another technique to increase the opacifying capicity of the light-reflective layer is to employ a separate opaque layer underneath it comprising, e.g., carbon black, nigrosine dyes, etc., dispersed in an alkaline solution-permeable polymeric matrix such as, for example, gelatin, polyvinyl alcohol, and the like. Such an opaque layer would generally have a density of at least 4 and preferably greater than 7 and would be substantially opaque to actinic radiation. The opaque layer may also be combined with a developer scavenger layer if one is present. The light-reflective and opaque layers are generally 1 to 6 mils in thickness, although they can be varied depending upon the opacifying agent employed, the degree of opacity desired, etc.

The supports of the film assemblies of this invention can be any material as long as it does not deleteriously affect the photographic properties of the film unit and is substantially dimensionally stable. Typical useful supports 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. In those embodiments where the support is transparent, it is usually about 2 to 6 mils in thickness and may contain an ultraviolet absorber for exposure control if desired. In addition, an adhesive layer able to be activated by the processing composition may be present on the support in order to increase its adhesion to the photosensitive element after processing.

The transparent support of the integral negative receiver film assemblies of this invention can be any of the materials mentioned above for the support. If desired, an ultraviolet-absorbing material can be employed in the support to prevent the dye images from fading dye to ultraviolet light.

The photosensitive substances used in this invention are preferably silver halide compositions and can comprise silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide and the like, or mixtures thereof. The emulsions may be course- or fine-grain and can be prepared by any of the well-known procedures, e.g., single-jet emulsions, double-jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in U.S. Pat. Nos. 2,222,264 by Nietz et al, 3,320,069 by Illingsworth, and 3,271,157 by McBride. Surface-image emulsions can be used or internal-image emulsions can be used such as those described in U.S. Pat. Nos. 2,592,250 by Davey et al, 3,206,313 by Porter et al, and 3,447,927 by Bacon et al. The emulsions may be regular-grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci., Vol.* 12, No. 5, Sept./Oct., 1964, pp. 242–251. If desired, mixtures of surface and internal-image emulsions can be used as described in Luckey et al, U.S. Pat. No. 2,996,382.

Negative-type emulsions can be used or direct-positive emulsions can be used such as those described in U.S. Pat. Nos. 2,184,013 by Leermakers, 2,541,472 by Kendall et al, 3,367,778 by Berriman, 3,501,307 by Illingsworth et al issued Mar. 17, 1970, 2,563,785 by Ives, 2,456,953 by Knott et al and 2,861,885 by Land, British Pat. Nos. 723,019 by Schouwenaars, and U.S. Ser. Nos. 123,005 by Evans filed Mar. 10, 1971, 123,006 by Milton filed Mar. 10, 1971, 123,007 by Gilman et al filed Mar. 10, 1971, 154,154 by Collier et al filed June 17, 1971, 154,155 by Gilman et al filed June 17, 1971, and 154,224 by Gilman et al filed June 17, 1971.

In a highly preferred embodiment, the imagewise-exposed photosensitive layers of the image transfer elements of this invention are developed in the presence of a development inhibitor-releasing compound. The development inhibitor-releasing compounds can be located in the layers of the photographic element in association with the silver halide emulsions or they can be provided by the alkaline processing solution in those instances where diffusible development inhibitor-releasing compounds are utilized. In one highly preferred embodiment, the development inhibitor-releasing compounds are those which contain a mercaptan development inhibitor thio-substituted on a hydroquinone. Typical useful compounds of this type are disclosed in U.S. Pat. Nos. 3,379,529 by Porter et al issued Apr. 23, 1968, and 3,364,022 by Barr issued Jan. 16, 1968, which are both incorporated herein by reference. The development inhibitor-releasing compounds are preferably incorporated in the layers of the element at concentrations of from 2 mg. to about 200 mg./ft.^{2}, and preferably from 5 mg. to 75 mg./ft^2. In a preferred embodiment, development inhibitor-releasing compounds such as 2,3-dimethyl-6-(1-phenyl-5-tetrazolylthio hydroquinone are utilized.

Generally, in the photographic elements referred to above, a positive image record is obtained in an image-receiving layer by mordanting the diffusible image-providing material which is not immobilized or remains nondiffusible in the photosensitive portion of the film unit. It is also appreciated that the photosensitive element contains an image record which provides a useful image product. In one instance, the mobile or diffusible materials can be washed out after exposure to produce an image dye record in the areas of silver halide developement. The silver halide emulsion can be selected to produce a negative image record or a positive image record in the photosensitive portion of the film element, for example, by using a negative or direct-positive silver halide emulsion.

The invention can be further illustrated by the following examples wherein the oxichromic compounds used are as identified above.

EXAMPLE 1

This example and Example 2 demonstrate in a nonimageforming format that certain preferred compounds of our invention having reduced azomethine linkages a) are essentially colorless when incorporated in a gelatinous coating composition, b) can be oxidized to an indophenol and c) can be converted by contact with a mordant, upon oxidation, to an image dye having desirable spectral properties.

A. A first sample of a supported single-layer gelatin machine coating, containing per square foot of coating 300 mg. gelatin, 50 mg. of Compound I and 150 mg. of diethyl lauramide, is spectrophotometrically evaluated. The coating appears essentially colorless. Quantitative sensitometric values are recorded in Table **1**, and the absorption profile of Compound I contained in the above coating sample is represented by Curve A in FIG. **1**.

B. A second sample of the above coating is soaked for 30 seconds at room temperature in an aqueous neutral oxidizing solution (pH 7.0) of $K_3Fe(CN)6$ and dried. The visual appearance of the so-treated sample is orange-yellow. Sensitometric values are recorded in Table 1, and the absorption profile of the indophenol is represented by Curve B in FIG. **1**.

C. A third sample of the coating described in Section (A) is soaked in an aqueous solution of hexadecyltrimethylammonium bromide at pH 7.0 and dried. The visual appearance of the so-treated coating sample is distinctly cyan. Aerial oxidation and simultaneous or subsequent contact of Compound I with the mordant apparently has brought about the desired change from colorless to cyan. Sensitometric values are recorded in Table **1**, and the absorption profile of the final cyan dye is represented by Curve C in FIG. **1**.

Table 1

Curve	Treatment	λmax (nm.)	Dmax
A	sample as coated	no distinct peak in visible region	0.08
B	$K_3Fe(CN)_6$	472	0.34
C	aqueous solution of hexadecyltrimethylammonium bromide, pH 7.0 (aerial oxidation)	625	1.08

EXAMPLE 2:

A. A first sample of a supported single-layer gelatinous hand coating, containing per square foot of coating 300 mg. gelatin, 50 mg. of Compound II and 150 mg. of diethyl lauramide, is spectrophotometrically evaluated. The coating appears essentially colorless. Quantitative sensitometric values are recorded in Table 2, and the absorption profile of Compound II contained in the above coating sample is represented by Curve A in FIG. **2**.

B. A second sample of the above coating is soaked for 30 seconds at room temperature in an aqueous neutral oxidizating solution (pH 7.0) of $K_3Fe(CN)_6$ and dried. The visual appearance of the so-treated sample is orange-yellow. Sensitometric values are recorded in Table 2, and the absorption profile of the indophenol is represented by Curve B in FIG. **2**.

C. A portion of the second sample treated by the procedure described in Section (B) above is soaked for 30 seconds at room temperature in an aqueous solution of hexadecyltrimethylammonium bromide at pH 12, then washed and dried. The visual appearance of the so-treated sample is distinctly cyan. In this instance, the more complete oxidation of the initially colorless compound by the $K_3Fe(CN)_6$ (vs. the partial oxidation by air as experienced during the process described in Example 3) is probably a factor in the subsequent production of the final cyan dye having a higher extinction coefficient. The treatment with the aqueous solution of hexadecyltrimethylammonium bromide at the higher pH (12.0 vs. 7.0) may also have been a factor in producing the higher dye density. Sensitometric values are recorded in Table 2, and the absorption profile of the final cyan dye is represented by Curve C in FIG. **2**.

Table 2

Curve	Treatment	λmax (nm.)	Dmax
A	sample as coated	no distinct peak in visible region	0.12
B	$K_3Fe(CN)_6$	485	0.40
C	$K_3Fe(CN)_6$ (plus aqueous solution of hexadecyltrimethylammonium bromide, pH 12)	636	2.08

EXAMPLE 3:

This example demonstrates in a nonimage-forming format the transfer, of an initially essentially colorless oxichromic developer to four receivers, each of which contains a different mordant. Oxidation of the oxichromic compound is effected by aerial oxidation upon separation of the matrix from the receiver.

A. A sample of the gelatin coating described in Section (A) of Example 2 (Compound II) is brought into intimate contact for 30 seconds with a receiver which contains a polyvinyl pyridine mordant in the presence of viscous processing liquid consisting of KOH and hydroxyethyl cellulose in water. Upon separation of the coating sample from the receiver, the latter is washed for 3 minutes with water.

B. The procedure described in Section (A) above is repeated with a receiver which contains a coacervate mordant of N-n-hexadecyl-N-morpholinium ethosulfate and methyl-tri-n-dodecylammonium p-toluenesulfonate.

C. The procedure described in Section (A) above is repeated with a receiver which contains the mordant copoly[styrene-(N,N-dimethyl-N-benzyl-N-3-maleiimidopropyl)ammonium]chloride.

D. The procedure described in Section (A) above is repeated with a receiver which contains the mordant N-n-octadecyl-tri-butylammonium bromide.

In each of the cases, Sections (A), (B), (C) and (D) above, a deep, intense cyan color forms upon separation of the receiver sheet from the matrix. The color is apparantly provided by aerial oxidation and the subsequent interaction between oxidized dye and mordant. The visual appearance of the final cyan dyes in each of the four receivers differs slightly, due to the varied nature of the individual mordant contained in each of the four receivers.

EXAMPLE 4:

A supported light-sensitive multilayer silver halide emulsion is made as follows:

1. support;
2. layer containing 300 mg./ft^2 gelatin, 50 mg./ft^2 Compound II and 150 mg./ft.^{2} diethyl lauramide;
3. layer containing silver halide with 250 mg./ft^2 of gelatin and 200 mg./ft.^{2} silver;
4. layer containing 80 mg./ft.^{2} gelatin.

A sample of the above-described coating is sensitometrically exposed through a graduated-density test object and then brought into intimate contact for 1 minute with a receiver containing the mordant N-n-octadecyl-tri-butylammonium bromide in the presence of the viscous processing fluid whose composition is shown below.

Processing Fluid

NaOH	20 g.
1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	0.75 g.
hydroxyethyl cellulose	25 g.
water to 1 liter	
pH 13.7	

Upon separation of the light-sensitive element from the receiver, the latter contains a well-defined cyan-colored reproduction of the test object.

EXAMPLE 5:

A first sample of a silver halide emulsion coating similar to that shown in Example 4, wherein the lowermost coating layer contains Compound I instead of Compound II according to this invention, is visually inspected. Its appearance is like that of a similar coating which does not contain the oxichromic developer, i.e., the oxichromic developer is essentially colorless. Only the yellow-tan of the silver halide emulsion is visible.

A second sample is subjected for 1 week to a heat fading test at a temperature of 49° C. (120° F.) and 20% r.h. Under the influence of the heat treatment, the appearance of the sample changes only slightly to a brown-yellow tan. It is apparent that the oxichromic developers according to our invention are relatively stable (i.e., resist oxidation) when contained in a stored silver halide emulsion coating prior to processing.

EXAMPLE 6:

A supported light-sensitive multilayer photographic element is made as follows:

1. support;
2. layer containing 300 mg./ft.^{2} of gelatin, 50 mg./ft.^{2} of Compound II and 150 mg./ft.^{2} diethyl lauramide;
3. layer containing silver halide emulsion at 100 mg./ft.^{2} of silver, 250 mg./ft.^{2} of gelatin and 10 mg./ft.^{2} 1-phenyl-3-pyrazolidone;
4. layer containing gelatin at 80 mg./ft.^{2} of gelatin.

A sample of the above-described coating is sensitometrically exposed through a graduated-density test object and then brought into intimate contact for 30 seconds with the mordant receiver N-n-octadecyl-tri-butylammonium bromide in the presence of the viscous processing fluid composed of:

NaOH	20 g.
1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	0.75 g.
hydroxyethyl cellulose	25 g.
water to 1 liter	
pH 13.7	

Upon separation of the two elements, the receiver contains a well-defined cyan-colored reproduction of the test object. The incorporation of an auxiliary developing agent in the lightsensitive matrix (in addition to the presence of a similar agent in the processing fluid) leads to an image of equally desirable sensitometric and improved incubation in the coated element.

EXAMPLE 7

A repeat of the procedures described in Example 6 with a processing fluid which consists of 40 g. KOH and 25 g. hydroxyethyl cellulose dissolved in 1 liter water leads to an equally desirable image.

EXAMPLE 8

Similar results are obtained when the procedures described in Example **6** are repeated with a mordanted receiver containing a coacervate of N-n-hexadecyl-N-morpholinium ethosulfate and methyl-tri-n-dodecylammonium p-toluenesulfonate and a mordanted receiver containing copoly[styrene-(N,N-dimethyl-N-benzyl-N-3-maleiimidopropyl)ammonium]chloride, respectively.

EXAMPLE 9

Photographic elements are prepared and tested as described in Example 1–A, 1–B and 1–C with the exception that Compound III is used instead of Compound I.

A. A first sample of a supported single-layer gelatin machine coating, containing per square foot of coating 300 mg. gelatin, 50 mg. of Compound III and 150 mg. of diethyl lauramide, is spectrophotometrically evaluated. Quantitative sensitometric values are recorded in Table **3**, and the absorption profile of Compound III contained in the above coating sample is represented by Curve A in FIG. **3.**

B. A second sample of the above coating is soaked for 30 seconds at room temperature in an aqueous neutral oxidizing solution (pH 7.0) of $K_3Fe(CN)6$ and dried. The visual appearance of the treated sample is moderately dense magenta. Sensitometric values are recorded in Table **3,** and the absorption profile of the indophenol by Curve B in FIG. **3.**

C. A third sample of the coating described in Section (A) is soaked in an aqueous solution of cetyltrimethylammonium bromide at pH 7.0 and dried. The visual appearance of the so-treated coating sample is distinctly magenta. Aerial oxidation and simultaneous or subsequent contact of Compound III with the mordant, an aqueous solution of cetyltrimethylammonium bromide, brings about the desired change from essentially colorless to magenta. Sensitometric values are recorded in Table 3, and the absorption profile of the magenta image dye is represented by Curve C in FIG. **3.**

Table 3

Curve	Treatment	λmax (nm.)	Dmax
A	sample as coated	slight peak in green region of spectrum	0.29
B	$K_3Fe(CN)_6$	527	1.82
C	aqueous solution of cetyltrimethyl ammonium bromide (aerial oxidation)	537	2.36

EXAMPLE 10

This example parallels Example 3 and demonstrates in a nonimage-forming format the transfer of the initially essentially colorless oxichromic developer Compound III to four receivers, each of which contains a different mordant. Oxidation of the oxichromic developer is effected by aerial oxidation upon separation of the matrix from the reciever.

Four separate samples of a gelatin coating containing Compound III, coated as described in Section (A) of Example 2, are brought into intimate contact for 30 seconds with strips of the receivers described in Example 3. Upon separation, the receivers are washed for 3 minutes with water.

Good magenta dyes are produced in each of the four receivers which differ slightly due to the varied nature of the individual mordant contained in the receivers.

EXAMPLE 11

A supported light-sensitive photographic element is coated as follows:

1. support;
2. layer containing 300 mg./ft.^{2} gelatin, 50 mg./ft.^{2} of Compound III and 150 mg./ft.^{2} of diethyl lauramide;
3. layer containing silver halide emulsion at 250 mg./ft.^{2} of gelatin, 100 mg./ft.^{2} of silver and 10 mg./ft.^{2} of 1-phenyl-3-pyrazolidone.

A sample of the above-described coating is sensitometrically exposed through a graduated-density test object and then brought into intimate contact for 1 minute with the mordanted receiver N-n-octadecyl-tri-butylammonium bromide in the presence of the processing fluid described in Example 4. The processing fluid also contains an auxiliary developing agent, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone.

Upon separation, the receiver contains a well-defined magenta-colored reproduction of the test object. Similar results are obtained when Compound IV is used in this photographic element.

EXAMPLE 12

Results similar to those described and illustrated in Example 3 are obtained when the transfers are executed in contact with the mordanted receivers, coacervate of N-n-hexadecyl-N-morpholinium ethosulfate and methyl-tri-n-dodecylammonium p-toluenesulfonate, and copoly[styrene-(N,N-dimethyl-N-benzyl-N-3-maleiimidopropyl)ammonium]chloride.

EXAMPLE 13

A sample of a supported single-layer gelatin machine coating, containing per square foot of coating 300 mg. gelatin, 50 mg. of Compound V and 100 mg. of diethyl lauramide, is visually inspected; the sample appears essentially colorless.

A supported light-sensitive photographic element is coated as follows:

1. support;
2. layer containing 300 mg./ft.^{2} of gelatin, 50 mg./ft.^{2} of Compound V and 100 mg./ft.^{2} of diethyl lauramide;
3. layer containing silver halide emulsion at 250 mg./ft.^{2} of gelatin, 10 mg./ft.^{2} of 1-phenyl-3-pyrazolidone and 100 mg./ft.^{2} of silver;
4. layer containing 80 mg./ft.^{2} gelatin.

A first sample of the above-described coating is sensitometrically exposed through a graduated-density test object and then contacted for 30 seconds with a mordanted receiver, a coacervate of N-n-hexadecyl-N-morpholinium ethosulfate and methyl-tri-n-dodecylammonium p-toluenesulfonate, in the presence of the processing fluid described in Example 4.

A second sample is processed similarly, but contacted for 60 seconds with a polyvinylpyridine mordanted receiver.

A third sample is processed similarly, but contacted for 60 seconds with a mordant receiver, N-n-octadecyl-tri-butylammonium bromide.

Upon separation of the three coating samples from the receivers, each of the latter contains a well-defined yellow colored reproduction of the photographed test object.

Similar results are obtained when Compounds VI, VII and VIII are used in this photographic element.

EXAMPLE 14

A. A first sample of a supported single-layer gelatin machine coating, containing per square foot of coating 300 mg. gelatin, 55 mg. of stabilized Compound IX and 50 mg. of diethyl lauramide, is visually inspected. The coating is clear and transparent; no color of any kind is visible.

B. A second sample of the coating described in Section (A) above is dipped into a neutral (pH 7.0) aqueous solution of $K_3Fe(CN)_6$. No change in the coating's appearance occurs; no color is produced.

A comparison of the observations described in Sections (A) and (B) above with samples containing the unstabilized oxichromic chromic dye clearly shows that less contamination occurs in an image transfer element with the stabilized oxichromic developers of this invention. The stabilized oxichromic developers appear to have improved resistance to produce color in a neutral-pH environment, such as prevails in a stored photographic element, and ease of conversion to undergo chromogenic oxidation to form dyes in the high-pH environment prevailing during an image transfer process.

The resistance to produce color at neutral-pH conditions is demonstrated above. The conversion to color at high-pH processing conditions is described in the following Examples 15, 16 and 17.

EXAMPLE 15

A supported light-sensitive photographic element is coated as follows:

1. support;
2. layer containing 300 ml./ft.^{2} of gelatin, 55 mg./ft^2 of Compound IX and 50 mg./ft.^{2} of diethyl lauramide;
3. layer containing negative silver halide emulsion at 250 mg./ft.^{2} of gelatin, 100 mg./ft.^{2} of silver and 10 mg./ft.^{2} of 1-phenyl-3-pyrazolidone;
4. layer containing 80 mg./ft.^{2} gelatin.

A sample of the above-described coating is sensitometrically exposed through a graduated-density test object and then brought into intimate contact for 30 seconds with a receiver containing the coacervate mordant N-n-hexadecyl-N-morpholinium ethosulfate and methyl-tri-n-dodecylammonium p-toluenesulfonate in the presence of the viscous processing fluid whose composition is shown below.

KOH	20 g.
hydroxyethyl cellulose	25 g.
water to 1 liter	
pH 13.7	

Upon separation of the light-sensitive element from the receiver, the latter contains a well-defined cyan-colored positive reproduction of the test object.

EXAMPLE 16

A supported single-layer, light-sensitive, photographic element is coated as follows:

1. support;
2. layer containing silver halide emulsion with 200 mg./ft.^{2} gel, 150 mg./ft.^{2} of silver, 50 mg./ft.^{2} Compound IX, 75 mg./ft.^{2} diethyl lauramide and 10 mg./ft.^{2} of 1-phenyl-3-pyrazolidone;
3. layer containing 80 mg./ft.^{2} gelatin.

A sample is exposed and contacted with a processing fluid and receiver as described in Example 15 with the production of a good cyan image.

EXAMPLE 17

Similar results are produced when the mordant N-n-hexadecyl-N-morpholinium ethosulfate and methyl-tri-n-dodecylammonium p-toluenesulfonate in the receiver of Example 15 is replaced with the mordant copoly[styrene-(N,N-dimethyl-N-benzyl-N3-maleiimidopropyl)ammonium] chloride.

EXAMPLE 18

Compound XXVIII is used according to the procedure of Example 15 with similar results.

EXAMPLE 19

Image separation in multicolor transfer units is demonstrated by the following coating and process.

A light-sensitive element is prepared with the following layers coated in sequence on a cellulose acetate film support of the specified concentrations per square foot:

1. a layer containing 100 mg. of a red-sensitive silver bromoiodide emulsion, 80 mg. of the stabilized oxichromic dye developer Compound IX 120 mg. of diethyl lauramide, 10 mg. of 1-phenyl-3-pyrazolidone and 125 mg. of gelatin;
2. an interlayer containing 250 mg. of gelatin, 70 mg. of 2,5-disec-dodecylhydroquinone as disclosed in Knechel, U.S. Ser. No. 17,330 filed Mar. 6, 1970, 72 mg. of diethyl lauramide, and 75 mg. of a yellow filter dye;
3. a layer containing 90 mg. of green-sensitive silver bromoiodide emulsion, 45 mg. of the oxichromic developer Compound XIII, 67 mg. of diethyl lauramide, 9 mg. of 1-phenyl-3-pyrazolidone and 100 mg. of gelatin;
4. an overcoat containing 80 mg. of gelatin.

A second light-sensitive element is coated as next above with the exception that the interlayer contains 195 mg. of diethyl lauramide and additionally contains 50 mg. of 2,3-dimethyl-6-(1-phenyl-5-tetrazolylthio)-hydroquinone.

The respective light-sensitive elements are imagewise-exposed and processed in contact for 60 seconds with a receiver sheet described in Example 2. A processing composition comprising 56 g. of KOH and 32 g. of hydroxyethyl cellulose added to 1 l. of water is uniformly spread between the photographic element and the receiver sheet by using a 0.002–0.003 inch undercut roller assembly.

At the end of the 60-second process, there is very little visible image dye in the receiver layer. However, a dense dye image appears with the respective colors after 3–5 seconds of exposure to air. The photographic element containing the 2,3-dimethyl-6-(1-phenyl-5-tetrazolylthio) hydroquinone in the interlayer produces the best density in the receiver layer with respect to the cyan dye (i.e., the blue and green exposure area).

The photographic element exhibits no substantial speed loss compared with a control element which does not contain the oxichromic developer, since the oxichromic developers are not dyes which absorb substantial radiation in the visible region of the electromagnetic spectrum.

EXAMPLE 20

In a multicolor image transfer film unit, the blue-sensitive silver halide emulsion associated with the yellow-forming oxichromic compound is preferably coated in the layer arrangement so that the other silver halide emulsion layers associated with oxichromic compounds are between the blue-sensitive emulsion layer and the image-receiving layer. In a highly preferred embodiment, the respective oxichromic compounds used in this format are stabilized oxichromic developers.

A photographic element is coated on a 4 mil polyethyleneterephthalate support with the following layers coated in sequence at the given concentrations per square foot:

1. layer containing 100 mg. gel, 60 mg. of Compound XIX, 90 mg. of N,N-diethyl lauramide and 0.75 mg. of bisvinyl sulfonyl methyl ether;

2. layer containing 70 mg. of gel, blue-sensitive silver halide at 90 mg. Ag/ft.^{2}, 10 mg. of 1-phenyl-3-pyrazolidone and 0.52 mg. of bis-vinyl sulfonyl methyl ether;

3. layer containing 200 mg. of gel, 20 mg. of **2,5**-di-sec-dodecylhydroquinone, 100 mg. of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-diamylphenoxyacetamide)benzamido]-4-(4-methoxyphenylazo)-5-pyrazolone and 1.5 mg. of bis-vinyl sulfonyl methyl ether;

4. layer containing 170 mg. of gel, green-sensitive silver halide emulsion at 50 mg. Ag/ft.^{2}, 50 mg. of Compound XVI, 75 mg. of N,N-diethyl lauramide, 10 mg. of 1-phenyl-3-pyrazolidone and 1.3 mg. of bis-vinyl sulfonyl methyl ether;

5. layer containing 200 mg. of gel, 20 mg. of 2,5-di-sec-dodecylhydroquinone, 30 mg. of 1-(2,4,6-trichlorophenyl-3)-3-[α-(3-pentadecylphenoxy)butyramido]benzamido-5-pyrazolone coupled with oxidized 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline, 1.5 mg. of bis-vinyl sulfonyl methyl ether and 25 mg. of 2,3-dimethyl-6-(1-phenyl-5-tetrazolylthio)hydroquinone;

6. layer containing 195 mg. of gelatin, a red-sensitive silver halide emulsion at 60 mg. Ag/ft.^{2}, 50 mg. of Compound IX, 75 mg. of N,N-diethyl lauramide, 10 mg. of 1-phenyl-3-pyrazolidone and 1.5 mg. of bis-vinyl sulfonyl methyl ether; and

7. layer containing 70 mg. of gelatin.

The light-sensitive element above is imagewise-exposed through the base and processed for 60 seconds in contact with a receiver sheet, as described in Example 3(D), with a processing composition composed of 56 g. of KOH and 32 g. of hydroxyethyl cellulose added to 1 l. of water. The processing composition is spread between the photographic element and the receiver sheet by using a 0.002–0.003 inch undercut roller assembly.

This image-receiving layer contains very little noticeable image dye after the 60 second process. However, a three-color, dense dye image appears after the image-receiving sheet is separated from the photosensitive element and exposed to air.

Upon repetition of the above exposure-and-processing step, we have found that the diffusion time necessary to produce transfer of the dye image-providing substance to the image-receiving layer s less than that required with dye developers used in a similar format wherein the dye developer is in a separate layer under the silver halide emulsion with respect to exposure direction.

EXAMPLE 21

In a highly preferred embodiment, the photographic element is coated with the image-receiving layer and the photosensitive layers on the same support.

A transparent 0.004 inch polyethyleneterephthalate support is coated with the following layers in sequence at the specified concentrations per square foot:

1. an image-receiving layer containing a coacervate of 22 mg. of methyl-tri-n-dodecylammonium p-toluenesulfonate and 150 mg. of N-n-hexyldecyl-N-morpholinium ethosulfate, and 743 mg. of gelatin;

2. a layer containing 300 mg. of gelatin, 3000 mg. of TiO_2 and 1.3 mg. of bis-vinyl sulfonyl methyl ether;

3. a layer containing 360 mg. of gelatin, 300 mg. of carbon black and 1.3 mg. of bis-vinyl sulfonyl methyl ether;

4. a stripping layer containing 500 mg. of unhardened polyvinyl alcohol;

5. layer **6** of Example 20;

6. layer **5** of Example 20;

7. layer **4** of Example 20;

8. layer **3** of Example 20;

9. layer **2** of Example 20;

10. layer **1** of Example 20; and

11. a gelatin overcoat containing 70 mg. of gelatin.

A transparent 0.004 inch polyester cover sheet is then superposed over the gelatin overcoat **11** and a rupturable pod is positioned to insert processing composition (made according to Example 20 with the addition of 10 g. per liter of carbon black) between the cover sheet and the photosensitive element to provide a film unit. The film unit is then imagewise-exposed through the cover sheet and the film unit is pulled through a pair of juxtaposed rollers to rupture the pod and distribute the processing composition. After spreading the processing composition, the film unit is brought into roomlight conditions for 60 seconds. The support containing the image-receiving layer is then peeled from the photosensitive layers at the stripping layer. After about 3 to 5 seconds, a dense, three-color image appears in the image-receiver layer which can be viewed through the support.

The stripping layer can be omitted and the film unit can be left laminated together to produce a good image record if an oxidizing agent is present in the image-receiving layer, for example, 100 mg./ft.^{2} of 1,4-didecyl-1,4-diazabicyclo-[2,2,2]-octanonium persulfate dissolved in dibutyl phthalate can be coated with the coacervate mordant to produce a good image upon transfer. An acid layer is generally present in the element to lower the pH after processing, especially when the unit remains laminated. In one preferred structure, a polyacrylic acid layer is coated on the cover sheet with a timing layer of polyvinyl acetate coated thereon. The acid layer will then neutralize the layers in the same order in which they were activated by the processing composition.

If desired, a separate pod or container means can also be used to insert an oxidizing agent into contact with the image-receiving layer after exposure of the film unit, or a transparent porous support can be used next to the image-receiving layer to allow sufficient air to provide for chromogenic oxidation of the oxichromic compound. However, in the preferred embodiments the oxidizing agent is incorporated in the image-receiving layer and is a compound which will not diffuse into the photosensitive layers.

EXAMPLE 22

This example demonstrates in a nonimaging format the transfer of Compound XIX to a receiver sheet containing the mordant N-n-octadecyl-tri-butylammonium bromide.

A sample is prepared according to Example 2(A) using Compound XIX instead of Compound II. The coating appears to be essentially colorless, with the quantitative sensitometric value recorded in FIG. **4** as in line A. The sample is then brought into contact for

30 seconds with the receiver sheet in the presence of a viscous processing liquid consisting of KOH and hydroxyethyl cellulose in water. After 3 to 5 seconds of separation, a dense yellow image is produced. The absorption characteristics of the image dye are shown as line C of FIG. 4.

EXAMPLE 23

An integral color transfer photographic element is prepared as follows (the full identification of certain components follows the example):

1. transparent polyethylene terephthalate support;
2. dye mordant layer containing gelatin at 100 mg./ft.^{2}, copoly[styrene/N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride] at 200 mg./ft.^{2} and a nitroxyl oxidant at 200 mg./ft.^{2};
3. layer containing titanium dioxide at 2000 mg./ft.^{2} and gelatin at 200 mg./ft.^{2};
4. layer containing carbon opacifying agent at 250 mg./ft.^{2} and gelatin at 156 mg./ft.^{2};
5. layer containing gelatin at 75 mg./ft.^{2}, 2,5-di-sec-dodecylhydroquinone at 70 mg./ft.^{2} and tricresyl phosphate at 23 mg./ft.^{2}. 6. layer containing a red-sensitive silver bromoiodide emulsion at 70 mg./ft.^{2} based on silver, gelatin at 230 mg./ft.^{2}, Compound X at 42 mg./ft.^{2} dispersed in diethyl lauramide at 73 mg./ft.^{2}, 5-(2-cyanoethylthio)-1-phenyltetrazole at 5 mg./ft.^{2} dispersed in tricresyl phosphate at 15 mg./ft.^{2} and 5,6,7,8-tetrahydro-5,8-methanol-1,4-naphthalenedion at 10 mg./ft.^{2};
7. layer containing gelatin at 300 mg./ft.^{2}, 2,5-di-sec-dodecylhydroquinone at 70 mg./ft.^{2} and a magenta filter dye at 30 mg./ft.^{2} dissolved in diethyl lauramide at 50 mg./ft.^{2};
8. layer containing green-sensitive silver bromoiodide emulsion at 70 mg./ft.^{2} based on silver, gelatin at 230 mg./ft.^{2}, Compound XVI at 54 mg./ft.^{2} dispersed in diethyl lauramide at 64 mg./ft.^{2}, 5-(2-cyanoethylthio)-1-phenyltetrazole at 5 mg./ft.^{2} dispersed in tricresyl phosphate and 5,6,7,8-tetrahydro-5,8-methano-1,4-naphthalenediol at 10 mg./ft.^{2};
9. layer containing gelatin at 300 mg./ft.^{2}, 2,5-di-sec-dodecylhydroquinone at 70 mg./ft.^{2} and a yellow filter dye at 100 mg./ft.^{2} dispersed in diethyl lauramide at 28 mg./ft.^{2};
10. layer containing a blue-sensitive silver bromoiodide emulsion at 70 mg./ft.^{2} based on silver, gelatin at 210 mg./ft.^{2}, Compound XXV at 64 mg./ft.^{2} dispersed in diethyl lauramide at 106 mg./ft.^{2}, 5-(2-cyanoethylthio)-1-phenyltetrazole at 5 mg./ft.^{2} dispersed in tricresyl phosphate at 15 mg./ft.^{2} and 5,6,7,8-tetrahydro-5,8-methano-1,4-naphthalenediol at 10 mg./ft.^{2};
11. layer containing gelatin at 50 mg./ft.^{2}.

A transparent cover sheet for the above element is prepared as follows:

1. transparent polyethylene terephthalate support;
2. layer containing gelatin at 900 mg./ft.^{2}, polyacrylic acid at 900 mg./ft.^{2} and imidazole at 760 mg./ft.^{2};
3. layer containing cellulose acetate at 1140 mg./ft.^{2} and copoly(styrene-maleic anhydride) at 60 mg./ft.^{2}.

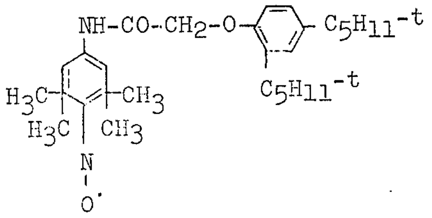
The photographic element is exposed through a multicolor, graduated-density test object, the transparent cover sheet superposed on the element, and a pod containing an opaque processing composition is ruptured to discharge between the cover sheet and the photosensitive element by passing the film unit through juxtaposed rollers having a gap of about 8 mils.

The processing composition is as follows:

potassium hydroxide	51 g./l.
hydroxyethyl cellulose	30 g./l.
potassium bromide	40 g./l.
α-benzylpicolinium bromide	15 g./l.
5,6,7,8-tetrahydro-5,8-methano-1,4-naphthalenediol	15 g./l.
carbon	40 g./l.

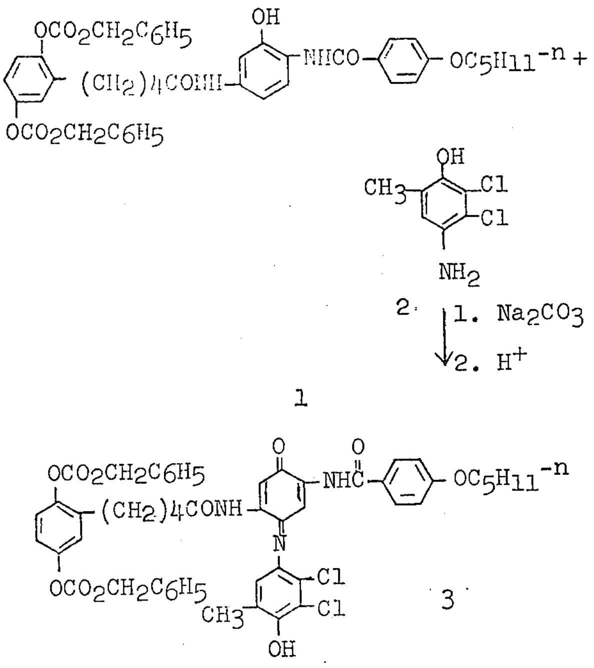
After about 1 to 2 minutes a well-defined color image with excellent color reproduction is viewed through the transparent support of the integral element.

The nitroxyl oxidant is the compound:

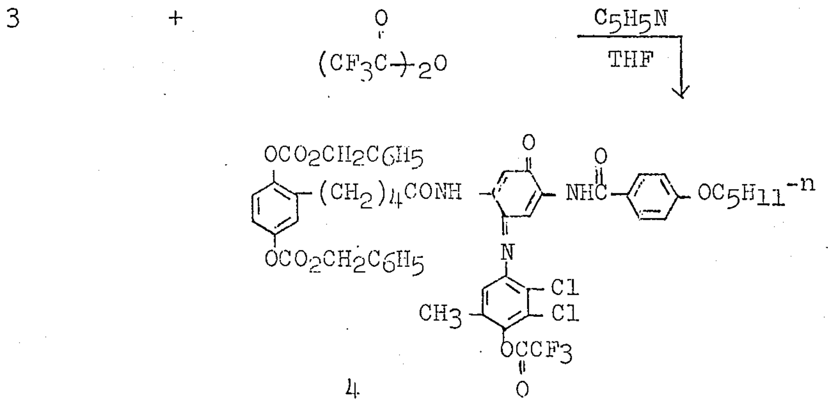


The nitroxyl oxidant can be made by reacting the respective ballasted acyl chloride with the 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl.

Compound X is prepared as follows:



A solution of 24 g. (0.03 mole) compound 1 and 11.7 g. (0.06 mole) compound 2 is added to a 5 l. Morton flask containing 90 g. Na_2CO_3 and 21 g. $(NH_4)_2S_2O_8$ dissolved in 1 l. H_2O. The mixture is stirred for 1½ hours and drowned in 10 l. H_2O containing 2 l. ethyl acetate. The ethyl acetate layer is separated, washed with water and then dilute acetic acid. The red solution is dried with $MgSO_4$, filtered and evaporated to give a red solid. The solid is strained over a fluorosil column ($CHCl_3$), then recrystallized from acetonitrile to give 20 g. red solid (m.p. 148°–150°C.).



Compound 3 is dissolved in 100 ml. of dry tetrahydrofuran containing 0.5 ml. dry pyridine, and 2 ml. of trifluoroacetic anhydride are then added. The solution immediately turns orange, is allowed to stand at room temperature for 1 hour and then dried. After recrystallization from acetonitrile, 4.7 g. of orange solid are collected (m.p. 152°–7° C.).

A 1 pint Parr bottle containing 150 ml. tetrahydrofuran, 1 g. Pd/C and 5 g. of compound 4 is reduced at room temperature for ½ hour at 35 lbs./in.^{2} of hydrogen. The mixture is filtered through celite to remove catalyst and the solvate is removed under reduced pressure to give a light pink solid. After recrystallization from acetonitrile, 3 g. of a white solid are collected (m.p. 187°–189° C.) which is Compound X.

EXAMPLE 24

An image transfer element is prepared as follows:

1. support;
2. layer containing a red-sensitive silver bromoiodide emulsion at 70 mg./ft.^{2} based on silver, gelatin at 230 mg./ft.^{2}, Compound XI at 75 mg./ft.^{2} dispersed in diethyl lauramide at 122 mg./ft.^{2}, 5,6,7,8tetrahydro-5,8-methano-1,4-naphthalenediol at 10 mg./ft.^{2}, and 5-(2-cyanoethylthio)-1-phenyltetrazole at 7.5 mg./ft.^{2} dispersed in tricresyl phosphate at 22 mg./ft.^{2};
3. layer containing gelatin at 150 mg./ft.^{2}, 2,5-di-sec-dodecylhydroquinone at 70 mg./ft.^{2}, a magenta filter dye at 30 mg./ft.^{2} dispersed in diethyl lauramide at 50 mg./ft.^{2};
4. layer containing a green-sensitive silver bromoiodide emulsion at 70 mg./ft.^{2} based on silver, gelatin at 230 mg./ft.^{2}, Compound XVI at 55 mg./ft.^{2} dispersed in diethyl lauramide at 65 mg./ft.^{2}, 5,6,7,8-tetrahydro-5,8-methano-1,4-naphthalenediol at 10 mg./ft.^{2}, and 5-(2-cyanoethylthio)-1-phenyltetrazole at 7.5 mg./ft.^{2} dispersed in diethyl lauramide at 22 mg./ft.^{2};
5. layer containing gelatin at 150 mg./ft.^{2}, 2,5-di-sec-dodecyl hydroquinone, a yellow filter dye at 100 mg./ft.^{2} dispersed in diethyl lauramide at 28 mg./ft.^{2};
6. layer containing a blue-sensitive silver bromoiodide emulsion at 70 mg./ft.^{2} based on silver, gelatin at 210 mg./ft.^{2}, Compound XXVI at 46 mg./ft.^{2} dispersed in diethyl lauramide at 79 mg./ft.^{2}, 5,6,7,8-tetrahydro-5,8-methano-1,4-naphthalenediol at 10 mg./ft.^{2}, and 5-(2-cyanoethylthio)-1-phenyltetrazole at 7.5 mg./ft.^{2} dispersed in tricresyl phosphate at 22 mg./ft.^{2};
7. layer containing gelatin at 50 mg./ft.^{2}.

The above photosensitive element is exposed through a multicolor, graduated-density test object and processed by rupturing a pod containing the following processing composition while in contact with a single-layer receiving element containing 200 mg./ft.^{2} copoly[styrene/N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride] and 200 mg./ft.^{2} gelatin.

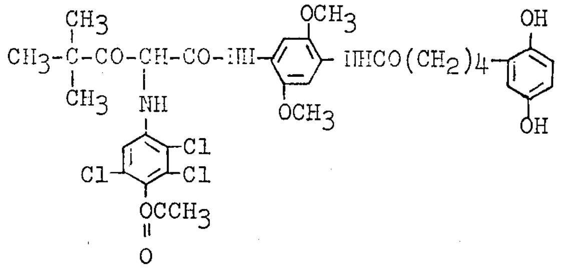
Processing Composition

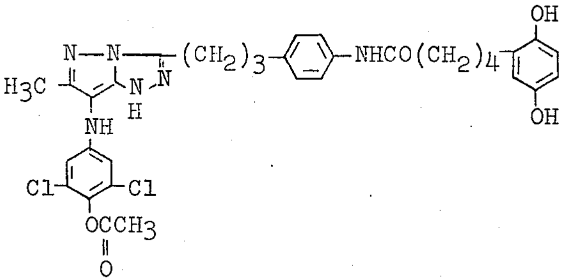
potassium hydroxide	51 g./l.
potassium bromide	50 g./l.
α-benzyl picolinium bromide	10 g./l.
hydroxyethyl cellulose	30 g./l.

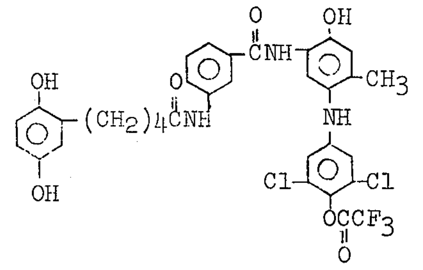
After 60 seconds and the photosensitive element and receiver are separated. A well-defined color image after about excellent color reproduction is observed after 1 minute of exposure to air where oxidation occurs.

The example is repeated where all of the 5,6,7,8-tetrahydro-5,8-methano-1,4-naphthalenediol is placed in the processing pod instead of the element. A well-defined image with good color reproduction is observed after processing.

Compounds XXVI, XVI and XI are as follows:

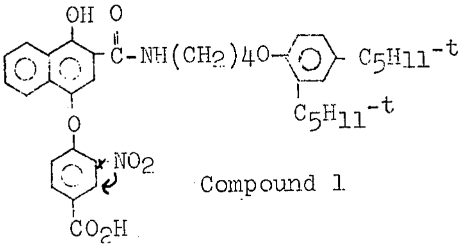






EXAMPLE 25

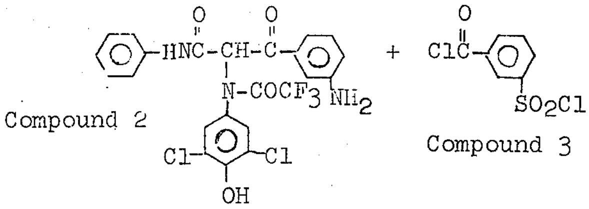
A ballasted oxichromic compound is prepared as follows:


Compound 1

Intermediate A

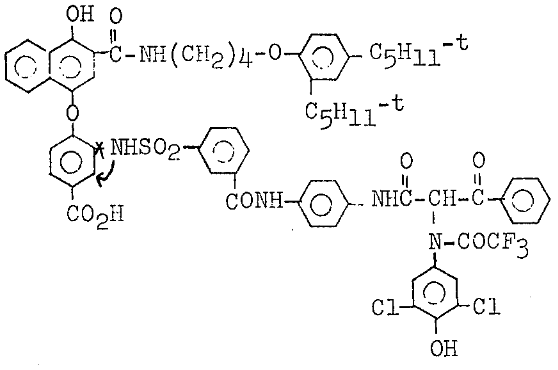
One equivalent of Compound 1, prepared in accordance with Loria, U.S. Pat. No. 3,476,563, is dissolved in 150 ml. of dry tetrahydrofuran in a Parr hydrogenation bottle containing 1 g. of Pd/C catalyst. The mixture is reduced at 45 lbs./in.^{2} hydrogen at 25° C. until 3 equivalents of hydrogen are taken up. The mixture is filtered to remove catalyst and the filtrate stripped to dryness, giving a solid which is recrystallized from acetonitrile to give a white solid.

Intermediate B:


Compound 2 Compound 3

One equivalent of Compound 2, prepared as described in Example 8 of Lestina and Bush, U.S. Ser. No. 206,949, is dissolved in 20X volume of acetic acid containing 1 equivalent of dissolved acetic acid. To this is added 1 equivalent of Compound 3 in granular form. The solution is stirred for 2 hours at room temperature, drowned in H_2O containing dissolved NaCl. A gummy solid is formed, collected and dissolved in ethyl acetate. The ethyl acetate is washed with H_2O, dried and removed under reduced pressure to give a tan solid which can be recrystallized from acetonitrile.

One equivalent each of Intermediates A and B are dissolved in 20X volume of dry acetone containing 1 equivalent of Na_2CO_3. The mixture is refluxed 16 hours, filtered, and acetone removed under pressure. A tar forms which crystallizes from chloroform and can be recrystallized from acetonitrile. The compound is believed to have the formula:



This compound is used in an image transfer film unit as described in Whitmore, U.S. Pat. No. 3,227,552, which employs direct-positive silver halide emulsions. The image-receiving layer contains the mordant N-n-octadecyl-tri-butylammonium bromide. Good yellow positive images are obtained in the receiver sheet after processing and air-oxidation of the receiver sheet.

Magenta and cyan image dye-providing ballasted oxichromic compounds can be provided by similar procedures using the appropriate oxichromic intermediate in the reaction with the ballasted coupler.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected with the spirit and scope of the invention.

We claim:

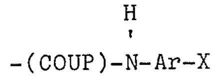
1. A photographic element comprising a support and at least one layer thereon containing a photographic silver halide composition having associated therewith 1) an oxichromic compound which is diffusible in an alkaline processing medium through organic colloid layers of said element and said compound has the formula:

$$D—(OC)$$

or 2) an oxichromic compound of the formula:

$$(OC)—LINK—(COUP^2—BALL)_n$$

wherein D is an aromatic group which is a silver halide developer; (OC) is a group which upon oxidation will form an imine dye chromophore and has the structure:



$$-(COUP)-\overset{H}{N}-Ar-X$$

wherein (COUP) is a color coupler connected to the nitrogen atom at its coupling position, Ar is an arylene group containing from 6 to 20 carbon atoms, and X is an amino group or an hydroxy group; LINK is a connecting radical which will split when contacted with an oxidized silver halide developer; COUP^2 is a coupler radical which is a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, said COUP^2 being substituted in the coupling position with said LINK; BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said compound nondiffusible during development in an alkaline processing composition; and *n* is an integer of 1 to 2.

2. A photographic element according to claim 1 wherein X is an hydroxy group.

3. A photographic element according to claim 2 wherein X is an hydroxy group and said element comprises at least one layer containing an 'onium salt in water-permeable association with said oxichromic compound.

4. A photographic element according to claim 1 wherein said oxichromic compound is diffusible in an alkaline processing composition and has said formula:

$$D—(OC)$$

5. A photographic element according to claim 4 wherein D comprises an aromatic nucleus which contains at least two substituents thereon from the class of hydroxy groups, amine groups or alkylamine groups.

6. A photographic element according to claim **4** wherein D is a hydroquinone group.

7. A photographic element according to claim **4** wherein (OC) is a reduced indophenol.

8. A photographic element according to claim **4** wherein (OC) is a stabilized oxichromic moiety containing O— or N— atoms having an acyl group thereon.

9. A photographic element according to claim **8** wherein said oxichromic group is N—stabilized by having a hydrolyzable acyl group attached to said N—atom.

10. A photographic element according to claim **8** wherein said oxichromic group is O—stabilized by having a hydrolyzable acyl group attached to said O—atom.

11. A photographic element according to claim **1** wherein said oxichromic compound has said formula:

(OC)—LINK—(COUP—BALL)$_n$

12. A photographic element according to claim **11** wherein (OC) contains water-solubilizing groups thereon.

13. A photographic element according to claim **11** wherein (OC) is an oxichromic group which is O— or N—stabilized with an acyl group.

14. A photographic element according to claim **1** wherein said element comprises at least two separate layers containing a silver halide emulsion, each having a different oxichromic compound associated therewith.

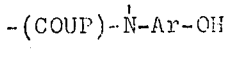
15. A photographic element according to claim **1** wherein said element comprises a blue-sensitive silver halide emulsion layer having associated therewith a yellow-forming oxichromic compound, a green-sensitive silver halide emulsion layer having associated therewith a magneta-forming oxichromic compound, and a red-sensitive silver halide emulsion having associated therewith a cyan-forming oxichromic compound.

16. A photographic element according to claim **15** wherein said cyan-forming oxichromic compound, said magenta-forming oxichromic compound and said yellow-forming oxichromic compound are each of said formula:

D—(OC)

and said element contains an image-receiving layer.

17. A photographic element according to claim **15** wherein said oxichromic compounds comprise an OC group having the formula:



$$-(\mathrm{COUP})-\overset{\mathrm{H}}{\mathrm{N}}-\mathrm{Ar}-\mathrm{OH}$$

wherein COUP is a color coupler and Ar is an arylene group.

18. A photographic element according to claim **17** wherein Ar is a phenylene group and said OH group is para to said nitrogen atom.

19. A photographic film unit comprising:

a. a photosensitive element comprising a support having thereon a layer containing a silver halide composition and having associated therewith an oxichromic compound of the formula:

(OC)—LINK—(COUP—BALL)$_n$

wherein (OC) is a group containing a reduced azomethine linkage; LINK is a connecting radical which is an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical, an azoxy radical, a sulfonamido radical, an aminoalkyl radical, a sulfonyl radical, a sulfonyloxy radical, an acyloxy radical or an imido radical; COUP is a coupler radical which is a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK; BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said compound nondiffusible during development in an alkaline processing composition; and *n* is an integer of 1 to 2;

b. a dye image-receiving layer; and

c. a means for discharging an alkaline processing composition within said film unit.

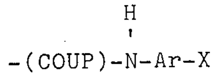
20. A photographic film unit according to claim **19** wherein said silver halide composition is a direct-positive silver halide emulsion.

21. 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 layer containing a silver halide composition and having associated therewith an oxichromic developer which is diffusible in alkaline processing media through organic colloid layers of said element and said developer has the formula:

D—(OC)

wherein D is an aromatic group which is a silver halide developer and (OC) is a group containing a reduced imine linkage which undergoes oxidation to form an imine dye chromophore and has the structure:



$$-(\mathrm{COUP})-\overset{\mathrm{H}}{\mathrm{N}}-\mathrm{Ar}-\mathrm{X}$$

wherein (COUP) is a color coupler connected to the nitrogen atom at its coupling position; Ar is an arylene group containing from 6 to 20 carbon atoms; and X is an amino group or an hydroxy group;

b. an image-receiving layer; and

c. a means for discharging an alkaline processing composition within said film unit.

22. The film unit of claim **21** wherein said image-receiving layer is located in said photosensitive element between said support and said silver halide composition layer.

23. A film unit according to claim **21** containing an 'onium salt in liquid-permeable association with said oxichromic developer and which is sequestered from said oxichromic developer until contact with said liquid processing composition.

24. The film unit of claim **21** wherein said photosensitive element comprises a support having thereon:

a. a red-sensitive silver halide emulsion layer having associated therewith a cyan-forming oxichromic developer;

b. a green-sensitive silver halide emulsion layer having associated therewith a magenta-forming oxichromic developer; and

c. a blue-sensitive silver halide emulsion layer having associated therewith a yellow-forming oxichromic developer.

25. A film unit according to claim **24** wherein said oxichromic developer contains a reduced indophenol moiety and said image-receiving layer comprises an 'onium compound.

26. A film unit according to claim **24** 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.

27. A film unit according to claim **24** wherein said image-receiving layer is coated adjacent said silver halide emulsion layers with an opaque layer between said silver halide emulsion layers and said image-receiving layer.

28. A film unit according to claim **21** having at least one layer containing a development inhibitor-releasing compound.

29. A film unit according to claim **21** wherein said discharging means comprises a rupturable container and is so positioned during processing of said film unit that a compressive force applied to said container by pressure-applying members will effect a discharge of the container's contents between said dye image-receiving layer and the layer most remote from the support of said photosensitive element.

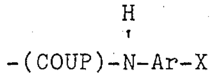
30. A film unit according to claim **21** wherein said discharging means comprises a rupturable container and is so positioned during processing of said film unit that a compressive force applied to said container by pressure-applying members will effect a discharge of the container's contents between the layer most remote from the support of said photosensitive element and a cover sheet superposed on said photosensitive element.

31. A process for producing a photographic transfer image comprising:

a. imagewise-exposing a photosensitive element comprising a support having thereon a silver halide composition layer having associated therewith an oxichromic developer which is diffusible in an alkaline processing composition through organic colloid layers and said developer has the formula:

$$D\text{—}(OC)$$

wherein D is an aromatic group which is a silver halide developer and (OC) is a group having the structure:



$$-(COUP)-\overset{H}{N}-Ar-X$$

wherein (COUP) is a color coupler connected to the nitrogen atom at its coupling position; Ar is an arylene group containing from 6 to 20 carbon atoms; and X is an amino group or an hydroxy group;

b. treating said photosensitive element with an alkaline processing composition to effect development of said exposed silver halide composition layer;

c. forming an imagewise distribution of diffusible oxichromic developer as a function of said imagewise exposure of said silver halide composition layer;

d. at least a portion of said imagewise distribution of diffusible oxichromic developer diffusing to an image-receiving layer; and

e. oxidizing said imagewise distribution of said oxichromic developer in said image-receiving layer.

32. A process according to claim **31** wherein said oxichromic developer is contacted with an 'onium compound after imagewise exposure.

33. A process according to claim **31** wherein said image-receiving layer contains an 'onium compound.

34. The process of claim **31** wherein said treatment step b) is effected by:

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

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

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

35. The process of claim **31** wherein said support is transparent and said image-receiving layer is located between said support and said silver halide composition layer, and said treatment is effected by applying a compressive force to a rupturable container located between the outermost layer of said photosensitive element and a transparent superposed cover sheet wherein said container an alkaline processing composition which is discharged by said compressive force.

36. A process according to claim **31** wherein at least one layer of said photographic element contains a development inhibitor-releasing compound.

37. A process according to claim **36** wherein said development inhibitor-releasing compound is a mercaptan development inhibitor thio-substituted on a hydroquinone.

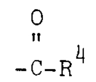
38. A process according to claim **31** wherein development of said exposed silver halide composition layer is carried out with an auxiliary developer present in said layer.

39. A photographic element comprising **1**) a support and **2**) at least one layer thereon containing a silver halide emulsion having associated therewith an oxichromic indophenol compound having a reduced azomethine linkage, which linkage is N- or O-stabilized with an acyl group by having a hydrolyzable acyl group attached to an O- or N- atom of said indophenol.

40. A photographic element according to claim **39** wherein said oxichromic compound is O-stabilized by having a hydrolyzable acyl group attached to an O-atom of said indophenol.

41. A photographic element according to claim **39** wherein said oxichromic compound is N-stabilized by having a hydrolyzable acyl group attached to the N-atom in said reduced azomethine linkage.

42. A photographic element according to claim **39** wherein said oxichromic compound is stabilized with an acyl group of the formula:

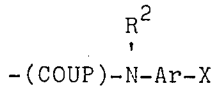


$$-\overset{\overset{\displaystyle O}{\|}}{C}-R^4$$

wherein R^4 is a halogenated alkyl group.

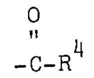
43. A photographic element according to claim **39** wherein said oxichromic compound is N-stabilized with a trifluoroacetate group.

44. In a photographic element comprising **1**) a support and **2**) at least one layer thereon containing a silver halide emulsion having associated therewith an oxichromic compound, the improvement wherein said oxichromic compound contains the group:



$$-(COUP)-\overset{\overset{\displaystyle R^2}{|}}{N}-Ar-X$$

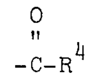
wherein (COUP) is a color coupler connected to the nitrogen atom at its coupling position; Ar is an arylene group containing from **6** to **20** carbon atoms; and X is an hydroxy group, an amino group or the group —O—R^1 wherein R^1 is a hydrolyzable acyl group



$$-\overset{\overset{\displaystyle O}{\|}}{C}-R^4$$

and R^2 is a hydrogen atom or the same substituent as R^1, provided that at least one of R^1 and R^2 is present as an acyl group.

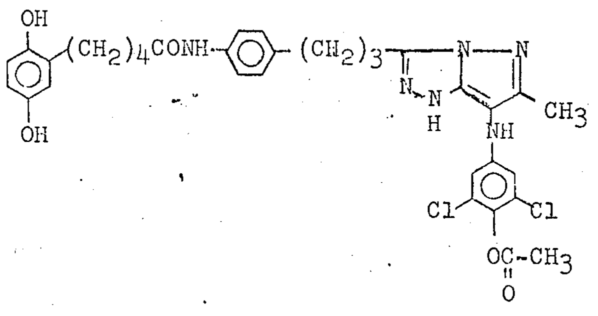
45. A photographic element according to claim **44** wherein said acyl group is a group of the formula:



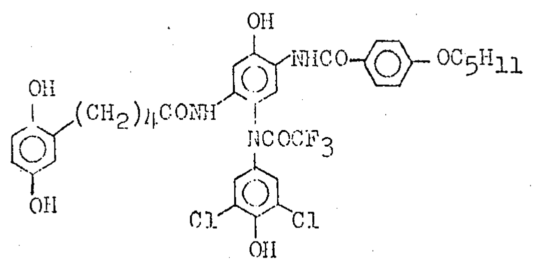
$$-\overset{\overset{\displaystyle O}{\|}}{C}-R^4$$

wherein R^4 is an alkyl group containing from 1 to 12 carbon atoms or a halogen-substituted alkyl group containing from 1 to 12 carbon atoms.

46. A photographic element according to claim **44** wherein said oxichromic compound is:



47. A photographic element according to claim **44** wherein said oxichromic compound is:



48. A photographic element according to claim **44** wherein said COUP is an open-chain ketomethylene coupler radical.

49. A photographic element according to claim **44** wherein said COUP is a **5**-pyrazolone coupler radical.

50. A photographic element according to claim **44** wherein said COUP is a pyrazolotriazole radical.

51. A photographic element according to claim **44** wherein said COUP is a phenolic coupler radical.

52. A photographic element according to claim **44** comprising an image-receiving layer located between said support and said layer containing said silver halide emulsion.

53. A film unit comprising a photographic element according to claim **52**, a transparent cover sheet superposed on the outermost silver halide layer and a means for discharging an aqueous processing composition between said cover sheet and said photographic element.

54. A photographic element according to claim **44** which contains a red-sensitive silver halide emulsion layer having associated therewith a cyan-forming oxichromic compound, a green-sensitive silver halide emulsion layer having associated therewith a magenta-forming oxichromic compound, and a blue-sensitive silver halide emulsion layer having associated therewith a yellow-forming oxichromic compound.

55. A photographic element according to claim **44** which contains at least one layer containing a development inhibitor-releasing compound.

56. In a photographic film unit comprising:

a. a photosensitive element comprising a transparent film support having coated thereon, in order:
  1. an image-receiving mordant layer,
  2. an alkaline solution-permeable, substantially opaque, light-reflective layer and
  3. layers comprising a red-sensitive silver halide composition layer having associated therewith a cyan dye-providing material, a green-sensitive silver halide composition layer having associated therewith a magenta dye-providing material, and a blue-sensitive silver halide composition layer having associated therewith a yellow dye-providing material;

b. a transparent cover sheet superposed over said layers containing a silver halide composition; and

c. means containing an alkaline processing composition having therein an opacifying agent, said means positioned to discharge said processing composition between said cover sheet and said layers containing silver halide compositions;

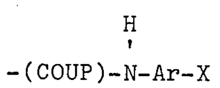
the improvement wherein each of said cyan, magenta and yellow dye-providing materials is an oxichromic compound which is diffusible in an alkaline processing medium through organic colloid layers of said element and said compound has the formula:

$$D—(OC)$$

or **2**) an oxichromic compound of the formula:

$$(OC)—LINK—(COUP^2—BALL)_n$$

wherein D is an aromatic group which is a silver halide developer; (OC) is a group which upon oxidation will form an imine dye chromophore and has the structure:



$$-(COUP)-\overset{\overset{\displaystyle H}{|}}{N}-Ar-X$$

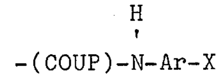
wherein (COUP) is a color coupler connected to the nitrogen atom at its coupling position, Ar is an arylene group containing from 6 to 20 carbon atoms, and X is an amino group or an hydroxy group; LINK is a connecting radical which will split when contacted with an oxidized silver halide developer; $COUP^2$ is a coupler radical which is a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, said $COUP^2$ being substituted in the coupling position with said LINK; BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said compound nondiffusible during development in an alkaline processing composition; and *n* is an integer of 1 to 2.

57. A film unit according to claim **56** wherein said layers of said photosensitive element are coated to position said blue-sensitive silver halide emulsion having associated therewith said yellow-forming oxichromic compound farther from said image-receiving layer than said green-sensitive silver halide composition layer or said red-sensitive silver halide composition layer.

58. A photographic film unit according to claim **56** wherein said dye-providing materials are oxichromic developers which are diffusible in said alkaline processing composition through organic colloid layers of said film unit and have the formula:

D—(OC)

wherein D is an aromatic group which is a silver halide developer and (OC) is a group containing a reduced azomethine linkage which upon oxidation will provide an imine dye chromophore and has the formula:



$$-(COUP)-\overset{H}{\overset{|}{N}}-Ar-X$$

wherein (COUP) is a color coupler connected to the nitrogen atom at its coupling position; Ar is an arylene group containing from 6 to 20 carbon atoms; and X is an amino group or an hydroxy group.

59. A photographic film unit according to claim **58** wherein said group containing said reduced azomethine linkage is O- or N-stabilized with a hydrolyzable acyl group.

60. A photographic film unit according to claim **56** which comprises at least one layer in said photosensitive element which contains a development inhibitor-releasing compound.

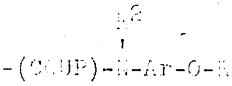
61. A film unit according to claim **56** wherein said alkaline solution-permeable, substantially opaque, light-reflective layer is a combination of a coating of titanium dioxide dispersed in a binder and a coating of carbon black dispersed in a binder with the titanium dioxide coating between the image-receiving layer and said coating containing carbon black.

62. A film unit according to claim **56** wherein said image-receiving layer has associated therewith an oxidizing agent.

63. A film unit according to claim **56** wherein said dye-providing materials have the formula:

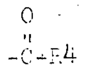
D—(OC)

wherein D is an aromatic nucleus which contains at least two hydroxy groups, and (OC) is an oxichromic group having the formula:



$$-(COUP)-\overset{R^2}{\overset{|}{N}}-Ar-O-R^1$$

wherein Ar is an arylene group containing from 6 to 20 carbon atoms; (COUP) is an open-chain ketomethylene color coupler, a phenolic color coupler, a pyrazolone color coupler or a pyrazolotriazole color coupler attached to said nitrogen atom in the coupling position; and R^1 and R^2 are hydrogen atoms or hydrolyzable carbonyl-containing groups of the formula:



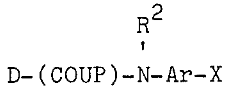
$$-\overset{O}{\overset{\|}{C}}-R^4$$

wherein R^4 is an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group.

64. A film unit according to claim **63** wherein at least one of R^1 and R^2 is said carbonyl-containing group.

65. A film unit according to claim **56** wherein said image-receiving layer has an 'onium compound associated therewith.

66. A photographic element comprising a support having thereon at least one layer containing a silver halide emulsion having associated therewith a stabilized oxichromic developer having the formula:



$$D-(COUP)-\overset{R^2}{\overset{|}{N}}-Ar-X$$

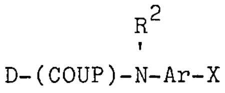
wherein (COUP) is a photographic color coupler linked to said nitrogen atom at the coupling position; D is an aromatic group which is capable of developing silver halide; Ar is an arylene group containing from 6 to about 20 carbon atoms; X is an hydroxy group or a group of the formula —O—R^1 wherein R^1 is a hydrolyzable acyl group; and R^2 is a hydrogen atom or the same substituent as R^1 provided that at least one of R^1 or R^2 is an acyl group.

67. A photographic element according to claim **66** comprising at least three separate layers containing silver halide emulsions which each have associated therewith an oxichromic developer of said formula.

68. A photographic element according to claim **66** wherein R^1 or R^2 are trifluoroacetyl groups.

69. 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 layer containing a silver halide emulsion having associated therewith a stabilized oxichromic developer having the formula:



$$D-(COUP)-\overset{R^2}{\overset{|}{N}}-Ar-X$$

wherein (COUP) is a photographic color coupler linked to said nitrogen atom at the coupling position; D is an aromatic group which is capable of developing silver halide; Ar is an arylene group containing from 6 to about 20 carbon atoms; X is an hydroxy group or a group of the formula —O—R^1 wherein R^1 is a hydrolyzable acyl group and R^2 is a hydrogen atom or the same substituent as R^1 provided that at least one or R^1 or R^2 is an acyl group;

b. an image-receiving layer; and

c. means for discharging an alkaline processing composition within said film unit.

70. A photographic film unit according to claim **69** wherein said photosensitive element comprises 1) a layer containing a blue-sensitive silver halide emulsion having associated therewith an oxichromic developer of said formula, 2) a layer containing a green-sensitive silver halide emulsion having associated therewith an oxichromic developer of said formula and 3) a layer containing a red-sensitive silver halide emulsion having associated therewith an oxichromic developer of said formula.

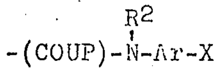
71. A photographic film unit according to claim **69** wherein said image-receiving layer comprises an 'onium salt.

72. A photographic film unit according to claim **69** wherein said image-receiving layer is located in said photosensitive element between said support and any said silver halide composition layer.

73. A film unit according to claim **69** wherein said image-receiving layer is located on a separate support and is adapted to be superposed on said photosensitive element.

74. A film unit according to claim **69** wherein COUP is a pyrazolone coupler, a pyrazolotriazole coupler, an open-chain ketomethylene coupler or a phenolic coupler.

75. A film unit according to claim **69** wherein said



$$-(\mathrm{COUP})-\overset{R^2}{\overset{|}{N}}-Ar-X$$

contains a reduced indophenol group.

* * * * *

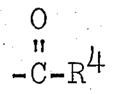
UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,880,658
DATED : April 29, 1975
INVENTOR(S) : Gregory James Lestina and Walter Monroe Bush

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

"acyl group", --,-- should be inserted; line 25:



" $-\overset{\overset{O}{\parallel}}{C}-R^4$ "

should be deleted.

Signed and Sealed this

twenty-fifth Day of *November 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks