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(54) Silver halide photographic material.

(57) A silver halide photographic material composed of a support having thereon at least one light-sensitive silver halide emulsion layer, at least one layer thereof containing at least one compound capable of releasing a foggant represented by formula (M-1) or (M-2) by a coupling reaction or a redox reaction with the oxidation product of a developing agent under alkaline conditions during development:

(M-1) $A - (L)\ell - Q'$

in which A represents a group to accelerate adsorbing to silver halide; L represents a divalent linking group; ℓ is 0 or 1; and Q′ represents a group derived from a quaternary salt nucleating agent represented by formula Q, by removing any hydrogen redical therefrom:

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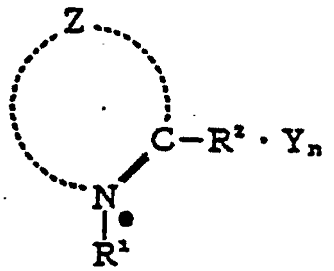
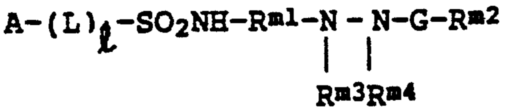


(Q)

where Z represents a substituted or unsubstituted non-metallic atomic group necessary for forming a 5- or 6-membered hetero-ring; R^1 represents a substituted or unsubstituted aliphatic group; R^2 represents hydrogen, a substituted or unsubstituted aliphatic group or substituted or unsubstituted and aromatic group, R^2 may be linked to Z to form a ring; provided that at least one of R^1, R^2 and Z contains an alkyl group, an acyl group, a hydrazine group or a hydrazone group, or R^1 and R^2 are linked to form a 6-membered dihydropyridinium ring; Y represents a counter ion necessary for charge balance; and n is 0 or 1; and

(M-2)



$$A-(L)_{\ell}-SO_2NH-R^{m1}-\underset{R^{m3}}{\underset{|}{N}}-\underset{R^{m4}}{\underset{|}{N}}-G-R^{m2}$$

in which R^{m1} represents a divalent atomic group; R^{m2} represents hydrogen, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, an aryloxy group or an amino group; G represents a carbonyl group, a sulfonyl group, a sulfoxy group, a phosphoryl group or an iminomethylene group; one of R^{m3} and R^{m4} is hydrogen, and the other hydrogen, an alkylsulfonyl group, an arylsulfonyl group or an acyl group; A represents a group accelerate the adsorbing to a silver halide; L represents a divalent linking group; and ℓ is 0 or 1. The material forms a direct positive image with a high maximum image density and a high resolving power. The material has a high storage stability even under high temperature and high humidity.

SILVER HALIDE PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic material which contains a compound capable of imagewise releasing a foggant by a coupling reaction or redox reaction with the oxidation product of a developing agent in at least one layer of the material.

BACKGROUND OF THE INVENTION

A silver halide color photographic material is known, which contains a coupler capable of releasing a development accelerator or a foggant by color development of the material. JP-A-57-150845 (the term "JP-A" as used herein means a "published, unexamined Japanese patent application") corresponding to US Patent 4,390,618, US Patent 4,518,682 and JP-A-59-170840 corresponding to US Patnet 4,628,024 illustrate couplers capable of releasing a foggant by reaction with the oxidation product of a color developing agent, and disclose that imagewise releasing of a foggant is effective for elevation of hard contrast in the images formed and for acceleration of development of photographic materials. In addition, compounds capable of imagewise releasing a foggant by a redox reaction with the oxidation product of a black-and-white developing agent, for example, hydroquinone, Metol or 3-pyrazolidone, in black-and-white development are disclosed in JP-A- 60-107029 corresponding to US Patent 4.724,199, which discloses that these compounds are effective for elevation of the sensitivity and hard contrast of negative emulsions. However, the effect of these compounds remains unsatisfactory.

On the other hand, in the case of direct formation of positive images by photo-fogging or chemical-fogging, since the developing speed is lower and the processing time is longer than for formation of conventional negative images a method of elevating the pH value of the developer used and/or the liquid temperature thereof so as to shorten the processing time has been employed. However, when the pH value of the developer is high, in general, there is a problem that the minimum image density of the direct positive image formed increases. In addition, the developing agent used is often deteriorated because of aerial oxidation under high pH conditions and, as a result, there is another problem that the developing activity of the developing agent is extremely reduced.

As other means of elevating the developing rate in the process of direct formation of positive images, use of hydroquinone derivatives (U.S. Patent 3,227,552) or carboxylic acid group- or sulfonic acid group-containing mercapto compounds (JP-A-60-170843) has been known. However, the effect attainable by the use of these compounds is insufficient, and a technique capable of effectively elevating the maximum density of direct positive images has not been found. In particular, a technique of obtaining a sufficient maximum image density by processing with a developer having a low pH value is desired.

In order to increase the maximum density of the direct positive images formed, core/shell type silver halide emulsions are often sensitized by surface chemical sensitization. However, excess chemical sensitization often causes an increase of the minimum density in the images formed, lowering of the sensitivity of the emulsion and formation of false images in the highly exposed part. In order to avoid these problems, the surface chemical sensitization must be stopped, in general, before a particular stage, and the surface chemically sensitized nuclei formed by the sensitization are weaker than those formed in conventional negative photographic materials. Accordingly, these positive photographic materials have an extremely poor time-dependent storage stability.

In order to overcome these drawbacks, a method of adding a stabilizer such as 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene or 1-phenyl-5-mercaptotetrazole, which has heretofore been well known, has been investigated. However, in order to prevent the variation of the photographic properties after storage, a large amount of the stabilizer must be added, and the addition of such a large amount of the stabilizer inevitably adversely affects the photographic properties. Specifio disadvantages include lowering of the maximum density of the positive images formed because of the action of the development inhibitor, elevation of the sensitivity of the re-reversed image, and interference in the adsorption of a sensitizing dye by the compound in spectral sensitization which is generally often applied to silver halide emulsions. Accordingly, a technique of overcoming these disadvantages and improving the time-dependent stability of the photographic materials is also desired.

Until now, it has been difficult to easily obtain direct positive color photographic materials which have a satisfactory maximum image density and which are excellent in the resolving power and the time-dependent stability.

SUMMARY OF THE INVENTION

A first object of the present invention is to provide a high contrast silver halide photographic material.

A second object of the present invention is to provide a silver halide photographic material which may be processed by an accelerated and rapid development process.

A third object of the present invention is to provide a silver halide photographic material having a high sensitivity.

A fourth object of the present invention is to provide a direct positive color photographic material capable of directly forming a positive image having a high maximum image density and a high resolving power.

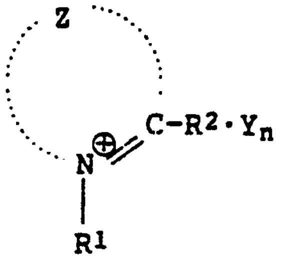
A fifth object of the present invention is to provide a direct positive color photographic material which is excellent in storage stability, especially in stability during storage in high temperature and high humidity conditions.

A sixth object of the present invention is to provide a direct positive color photographic material forming a direct positive image having a sufficiently high color density even when processed with a highly stable developer having a low pH value.

It has now been found that these and other objects can be attained by a silver halide photographic material composed of a support having thereon at least one light sensitive silver halide emulsion layer, at least one layer thereof containing at least one compound capable of releasing a foggant represented by formulae (M-1) or (M-2) by at least one of a coupling reaction and a redox reaction with the oxidation product of a developing agent under alkaline conditions during development:

(M-1) $A\text{-}(L)_{\ell}\text{-}Q'$

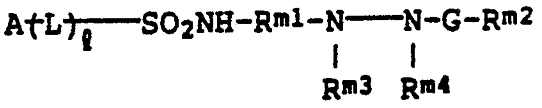
in which A represents a group promoting the adsorbing to a silver halide;
L represents a divalent linking group;
ℓ is 0 or 1;
Q' represents a group derived from a quaternary salt nucleating agent represented by formula Q, by removing any hydrogen radical which bonds to Q:



(Q)

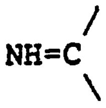
wherein Z represents a substituted or unsubstituted non-metallic atomic group necessary for forming a 5-membered or 6-membered hetero-ring;
R^1 represents a substituted or unsubstituted aliphatic group;
R^2 represents hydrogen, a substituted or unsubstituted aliphatic group or a substituted or unsubstituted aromatic group, and R^2 may be linked to Z to form a ring; provided that at least one of R^1, R^2 and Z contains an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or R^1 and R^2 are linked to form a 6-membered dihydropyridinium ring
Y represents a counter ion required for charge balance;
and n is 0 or 1; and

(M-2)



$$A\!-\!(L)_{\ell}\!-\!SO_2NH\!-\!R^{m1}\!-\!\underset{R^{m3}}{N}\!-\!\underset{R^{m4}}{N}\!-\!G\!-\!R^{m2}$$

in which R^{m1} represents a divalent aromatic group; R^{m2} represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, an aryloxy group or an amino group;
G represents a carbonyl group, a sulfonyl group, a sulfoxy group, a phosphoryl group or an iminomethylene group



;

one of R^{m3} and R^{m4} represents hydrogen, and the other represents hydrogen, an alkylsulfonyl group, an arylsulfonyl group or an acyl group;
A represents a group promoting the adsorbing to a silver halide;
L represents a divalent linking group; and
ℓ is 0 or 1.

DETAILED DESCRIPTION OF THE INVENTION

The compounds which may be used in the present invention include the following compounds (i) to (iii):

(i) A coupler capable of releasing the compound of the formula (M-1) or (M-2) or a precursor thereof by coupling with the oxidation product of an aromatic primary amine developing agent.

(ii) A coupler capable of releasing a diffusible coupling product by coupling with the oxidation product of an aromatic primary amine developing agent, the coupling product having a function of the compound of formula (M-1) or (M-2) or a precursor thereof.

(iii) A redox compound capable of releasing the compound of formula (M-1) or (M-2) or a precursor thereof by redox reaction with the oxidation product with a developing agent or by a successive reaction to follow the redox reaction.

"Precursor" disclosed above means a compound wherein a group of $-\!\!-\!(TIME)_m$ is attached to the compound of formula (M-1) or (M-2).

The above-mentioned compounds (i), (ii) and (iii) include those represented by the following formulae (1), (2) and (3), respectively.

[1] $Cp\text{-}(TIME)_m\text{-}M'$
[2] $BALL\text{-}Cp\text{-}(TIME)_m\text{-}M'$
[3] $RED\text{-}(TIME)_m\text{-}M'$

In the above formula, Cp represents a coupler capable of reacting with the oxidation product of an aromatic primary amine developing agent by coupling reaction to release $\text{-}(TIME)_m\text{-}M'$ or -BALL;
BALL represents a non-diffusible group capable of being released from Cp by a coupling reaction with the oxidation product of an aromatic primary amine developing agent;
RED represents a group capable of reacting with the oxidation product of a developing agent by a reaction to release $\text{-}(TIME)_m\text{-}M'$;
TIME represents a timing group capable of releasing M' after being released from Cp or RED by coupling reaction;
m is 0 or 1;
M' represents a group capable of being released from Cp or RED when m is 0, or M' represents a group capable of being released from TIME when m is 1; and
M' represents a group derived from the compound of the formula (M-1) or (M-2) by removing any hydrogen radical therefrom, and preferably linked to TIME, Cp or RED via A.

In formula (1), the group $\text{-}(TIME)_m\text{-}M'$ is bonded to the coupling position of Cp, and the bond is cleaved by coupling reaction.

In formula, (2), BALL is bonded to the coupling position of Cp, and the bond is cleaved by coupling reaction. Since the group $\text{-}(TIME)_m\text{-}M'$ is bonded to the non-coupling position of Cp, the bond is not directly cleaved by coupling reaction.

In formula (3), the group -(TIME)$_m$-M$'$ is bonded to a position capable of being released from RED by a redox reaction of RED with the oxidation product of a developing agent, or a successive reaction following the redox reaction.

The group TIME may be a trivalent group in formula (1). Specifically, one of the three bonds of the trivalent group TIME is bonded to M$'$, one of the remaining two bonds is bonded to the coupling position of Cp and the other one is bonded to the non-coupling position of Cp. As a characteristic feature of the compounds having such structure, the bond between TIME and the coupling position of Cp is cleaved by a coupling reaction with an aromatic primary amine developing agent, while the bond between TIME and the non-coupling position of Cp is not cleaved by the coupling reaction. The cleaved bond (anion) of TIME then causes cleavage of the bond between TIME and M$'$ by intramolecular electron transfer and/or an intramolecular nucleophilic substitution reaction in TIME, thereby to release M$'$ from TIME. Accordingly, in the case of such compounds, not only the group of TIME is merely a trivalent group, but also it is required to have a structure capable of releasing M$'$ therefrom by intramolecular electron transfer and/or intramolecular nucleophilic substitution reaction.

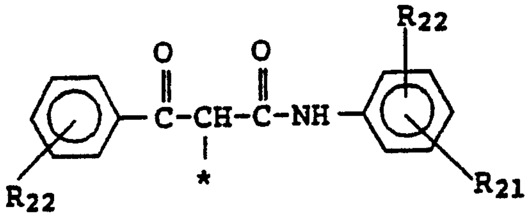
The preferred example of the group TIME is disclosed in JP-A-61-230935.

The compounds of the formulae (1), (2), and (3) will be explained in greater detail hereunder.

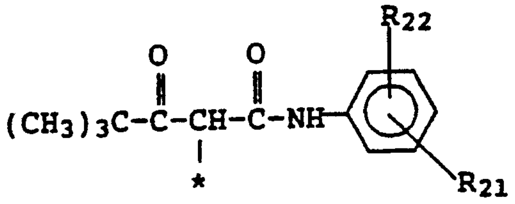
In the formula (1), the coupler residue represented by Cp can be any of yellow, magenta or cyan couplers, colorless couplers or black-coloring couplers, which are described below.

Among these couplers, specific examples of yellow couplers are described in U.S. Patents 2,875,057, 2,407,210, 3,265,506, 2,298,443, 3,048,194, and 3,447,928. Of the yellow couplers described, acylacetamide derivatives such as benzoylacetanilide and pivaloylacetanilide are preferred.

Accordingly, the yellow coupler residue (Cp) preferably is represented by formulae (Ia) and (IIa):



[Ia]



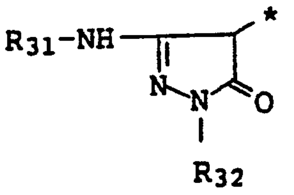
[IIa]

In these and the following formulae, * indicates the position to which the group -(TIME)$_m$-M$'$ is bonded in formulas (1), and (3), and the position to which -BALL is bonded in formula (2).

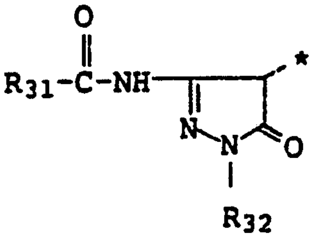
R_{21} represents a non-diffusible group in which the number of the total carbon atoms is from 8 to 32; R_{22} represents hydrogen or at least one substituent, preferably from 2 to 5 substituents and more preferably from 2 to 3 substituents, selected from a halogen atom, a lower alkyl group, a lower alkoxy group and a non-diffusible group in which the number of the total carbon atoms is from 8 to 32, and plural R_{22} groups may be the same or different.

Specific examples of magenta couplers represented by Cp for use in the present invention are described in U.S. Patents 2,600,788, 2,369,489, 2,343,703, 2,311,082, 3,152,896, 3,519,429, 3,062,653, 2,908,573, JP-B-47-27411, and JP-A-59-171956, JP-A-59-162548, JP-A-60-3352, JP-A-60-43659, and JP-A-60-172982. (The term "JP-B" as used herein refers to an "examined Japanese patent publication"). Of the magenta couplers described, pyrazolones or pyrazoloazoles (e.g., pyrazolopyrazoles, pyrazoloimidazoles, pyrazolotriazoles, pyrazolotetrazoles) are preferred.

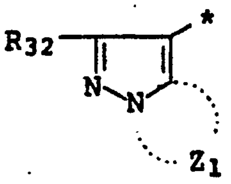
Accordingly, preferred magenta coupler residue (Cp) are represented by formulae (IIIa), (IVa) and (Va):



[IIIa]



[IVa]

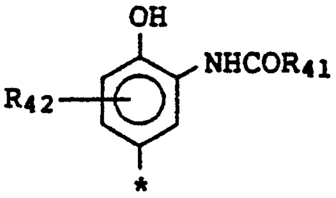


[Va]

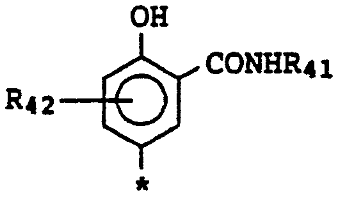
In these formulae, R_{31} represents a non-diffusible group in which the number of the total carbon atoms is from 8 to 32; R_{32} represents at least one substituent selected from a halogen atom, a lower alkyl group, a lower alkoxy group, a phenyl group and a substituted phenyl group; Z_1 represents a substituted or unsubstituted non-metallic atomic group necessary for forming a 5-membered azole ring containing from 2 to 4 nitrogen atoms, or a condensed ring thereof.

Specific examples of cyan couplers (Cp) are described in U.S. Patents 2,772,162, 2,895,826, 3,002,836, 3,034,892, 2,474,293, 2,423,730, 2,367,531, 3,041,236, JP-A-56-99341, JP-A-57-155538, JP-A-57-204545, JP-A-58-189154, JP-A-59-31953, JP-A-58-118643, JP-A-58-187928, JP-A-58-213748, U.S. Patent 4,333,999, etc. Of the cyan couplers described, phenols and naphthols are preferred.

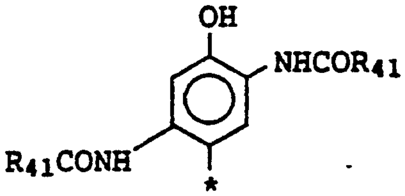
Accordingly, preferred cyan coupler residues (Cp) are represented by formulae (VIa), (VIIa), (VIIIa) and (IXa):



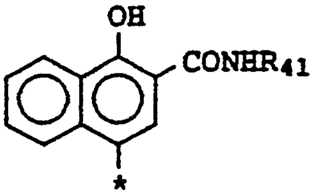
[VIa]



[VIIa]



[VIIIa]



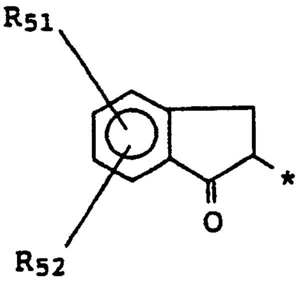
[IXa]

In these formulae, R_{41} represents a non-diffusible group in which the number of the total carbon atoms is from 8 to 32; R_{42} represents at least one substituent selected from a halogen atom, a lower alkyl group and a lower alkoxy group, and plural R_{42} groups may be the same or different.

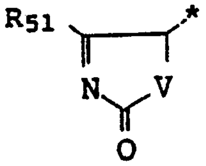
In addition, the residue Cp may also be a colorless coupler residue.

Specific examples of colorless couplers are described in U.S. Patents 3,912,513, 4,204,867, and JP-A-52-152721.

Specific examples of the colorless coupler residues (Cp) are represented by formulae (Xa), (XIa) or (XIIa):

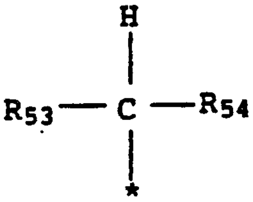


[Xa]



[XIa]

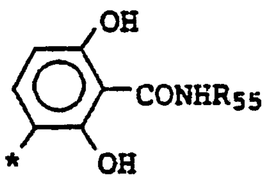
where R_{51} represents a non-diffusible group in which the number of the total carbon atoms is from 8 to 32; R_{52} represents hydrogen, a halogen, a lower alkyl group or a lower alkoxy group; and V represents oxygen, sulfur or nitrogen.



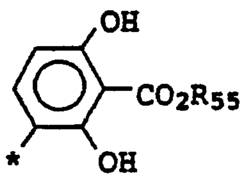
[XIIa]

where R_{53} and R_{54} which may be the same or different, each represents an alkoxycarbonyl group, an aminocarbonyl group, an acyl group or a sulfonic acid or sulfinic acid derivative of each group; a cyano group; an ammonium group; or a nitrogen-containing heterocyclic group linked to C via a nitrogen thereof; and R_{53} and R_{54} may be linked to form a 5-membered or 6-membered ring.

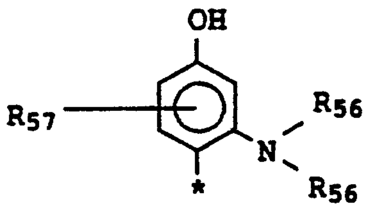
In addition the group (Cp) may also be a coupler residue capable of becoming black by reaction with the oxidation product of a developing agent. Examples of such couplers are described in U.S. Patents 1,939,231, 2,181,944, 2,333,106, 4,126,461, West German Patents Application (OLS) 2,644,194, and 2,650,764. Specific ally, such coupler residues (Cp) are represented by formulae (XIIIa), (XIVa) and (XVa):



[XIIIa]



[XIVa]



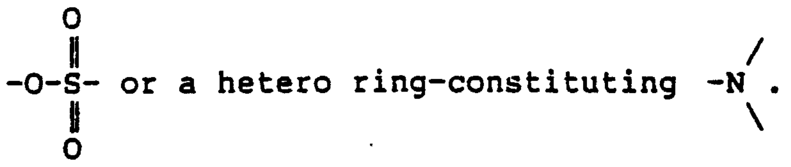
[XVa]

In these formulae, R_{55} represents an alkyl group having from 3 to 20 carbon atoms, an unsubstituted phenyl group or a phenyl group substituted with at least one hydroxyl group, halogen atom, amino group, alkyl group having from 1 to 20 carbon atoms or alkoxy group;
R_{56} represents a hydrogen atom, a halogen atom, an alkyl or alkenyl group having from 1 to 20 carbon atoms or an aryl group having from 6 to 20 carbon atoms;
R_{57} represents at least one halogen atom, an alkyl or alkoxy group having from 1 to 20 carbon atoms or a monovalent organic group, and plural R_{57} groups may be the same or different.

The residue (Cp) represented by any one of formulae [Ia] through [XVa] may form a dimer or higher polymer at any position except the coupling position, or it may be bonded to a polymer at any position except the coupling position.

In formula (2), the coupler residue represented by Cp is represented by any one of formulae [Ia] to [XVa]; BALL is bonded to the position marked by (*) in the formulae, and the group $-(TIME)_m-M'$ is bonded to any other position than the position bonded to BALL.

In formula (2), the non-diffusible group represented by BALL has a sufficient size and shape to impart nondiffusibility to the coupler, and it may be a polymeric group having plural releasable groups bonded thereto or may be a group having an alkyl group and/or an aryl group capable of imparting nondiffusibility to the coupler. In the latter case, the number of the total carbon atoms in the alkyl group and/or the aryl group is preferably from 8 to 32. BALL is bonded to the coupling position of Cp by a linking group, and specific examples of such group include -O-, -S-, -N = N-, $-O-\overset{O}{\overset{\|}{C}}-$,



$$-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}- \text{ or a hetero ring-constituting } -N\big< .$$

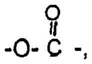
Preferable examples of BALL are disclosed, for example, in US Patents 3,358,700; 4,266,019; 4,232,312; 4,513,082; 3,894,895 and 3,664,841.

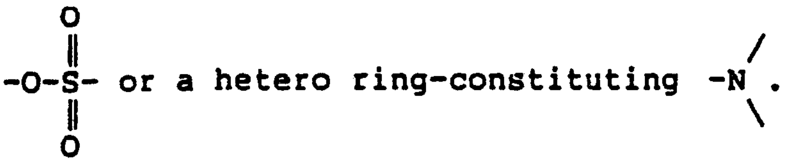
In the formula (3), the group represented by RED contains a hydroquinone, catechol, o-aminophenol or p-aminophenyl group, and this is a group which may react with the oxidation product of a developing agent (redox reaction) and then successively hydrolyzed under alkaline conditions monovalent organic group, and plural R_{57} groups may be the same or different.

The residue (Cp) represented by any one of formulae [Ia] through [XVa] may form a dimer or higher polymer at any position except the coupling position, or it may be bonded to a polymer at any position except the coupling position.

In formula (2), the coupler residue represented by Cp is represented by any one of formulae [Ia] to [XVa]; BALL is bonded to the position marked by (*) in the formulae, and the group -(TIME)$_m$-M$'$ is bonded to any other position than the position bonded to BALL.

In formula (2), the non-diffusible group represented by BALL has a sufficient size and shape to impart nondiffusibility to the coupler, and it may be a polymeric group having plural releasable groups bonded thereto or may be a group having an alkyl group and/or an aryl group capable of imparting nondiffusibility to the coupler. In the latter case, the number of the total carbon atoms in the alkyl group and/or the aryl group is preferably from 8 to 32. BALL is bonded to the coupling position of Cp by a linking group, and specific examples of such group include -O-, -S-, -N = N-,

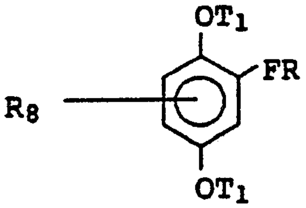

$-O-\overset{O}{\overset{\parallel}{C}}-$,


$-O-\overset{O}{\underset{O}{\overset{\parallel}{\underset{\parallel}{S}}}}-$ or a hetero ring-constituting $-N<$.

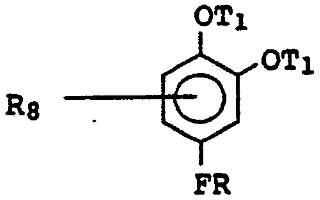
Preferable examples of BALL are disclosed, for example, in US Patents 3,358,700; 4,266,019; 4,232,312; 4,513,082; 3,894,895 and 3,664,841.

In the formula (3), the group represented by RED contains a hydroquinone, catechol, o-aminophenol or p-aminophenyl group, and this is a group which may react with the oxidation product of a developing agent (redox reaction) and then successively hydrolyzed under alkaline conditions to release the group -(TIME)m-M$'$. Preferable examples of RED are disclosed, for example, in US Patents, 3,930,863; 4,108,663; 4,345,024; and 3,825,426, and JP-A-61-230135. The group -(TIME)m-M$'$ is represented by FR in the following formulae (XVIa) to (XXIa).

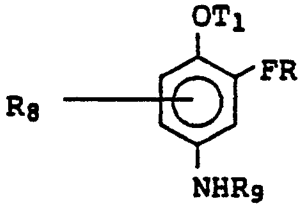
Specific examples of the group (RED) are represented by formulae (XVIa) to (XXIa):



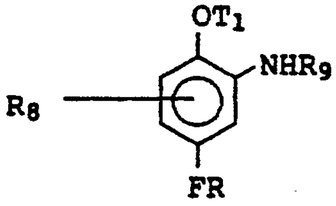
[XVIa]



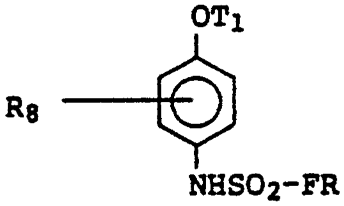
[XVIIa]



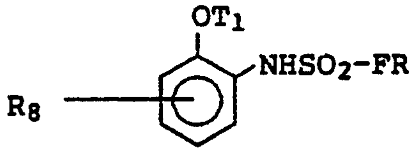
[XVIIIa]



[XIXa]



[XXa]



[XXIa]

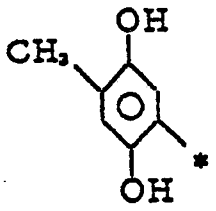
In these formulae, R_8 represents at least one hydrogen, a halogen, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a cyano group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, a carboxyl group, a sulfo group, a sulfonyl group, an acyl group, a carbonamido group, a sulfonamido group, a hydroxyl group, an acyloxy group or a heterocyclic group, and plural R_8 groups may be same or different, and two or more R_8 group may be linked to form a ring.

T_1 is a group in which a bond of $-O-T_1$ is cleaved during development processing to release $-O^-$, including for example, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, 2-cyanoethyl group, 2-methanesulfonylethyl group, etc.

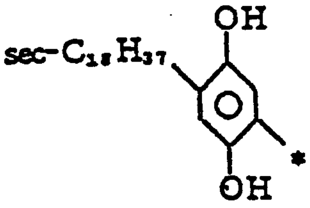
R^9 represents an acyl group or a sulfonyl group.

Preferred examples of compounds represented by formulae (XVIa) to (XXIa) are mentioned below. In the following structural formulae, (*) means the position to which the group FR is bonded.

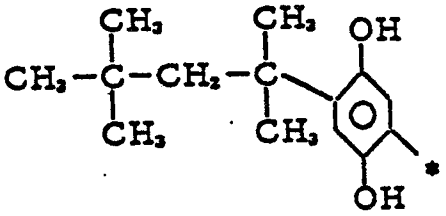
(1)



(2)



(3)



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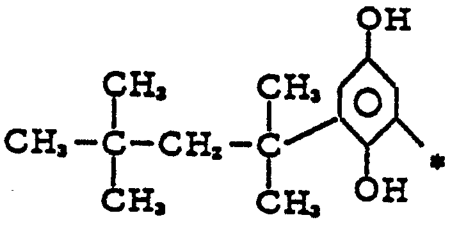
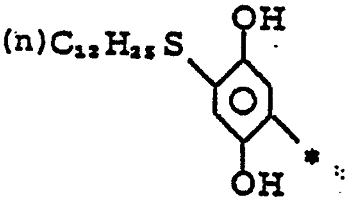


(5)



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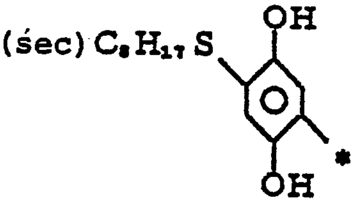

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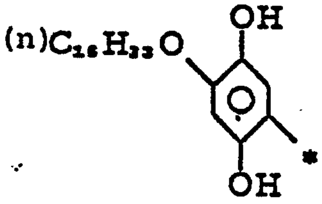

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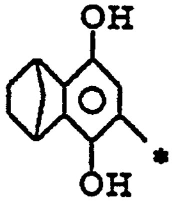

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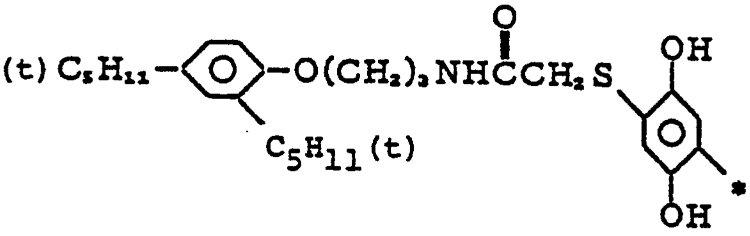

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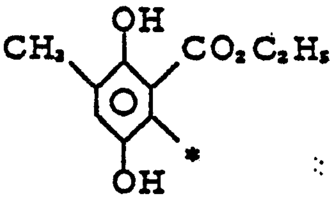

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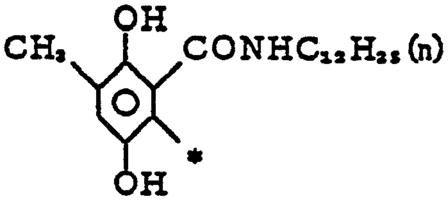

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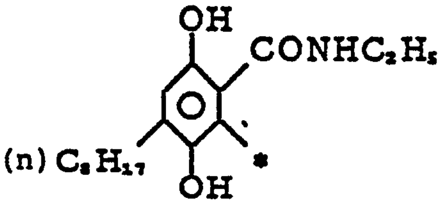

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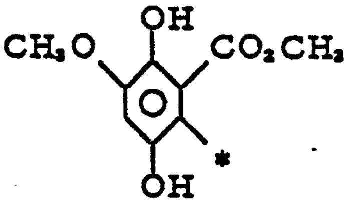

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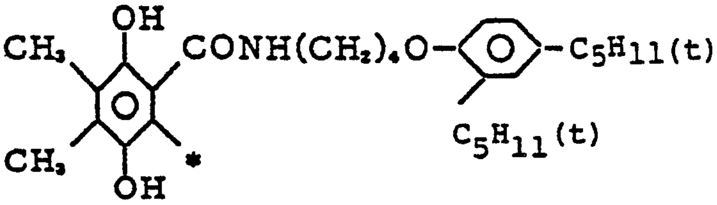

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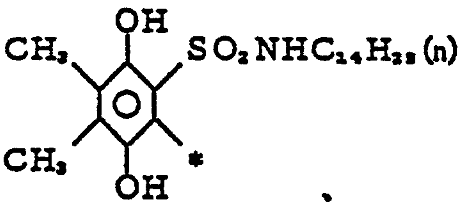

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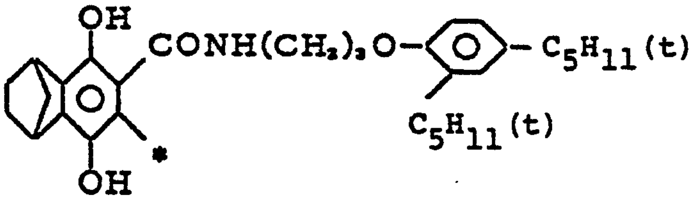

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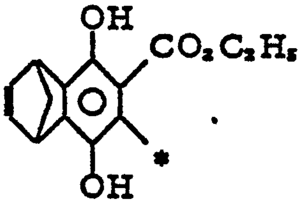

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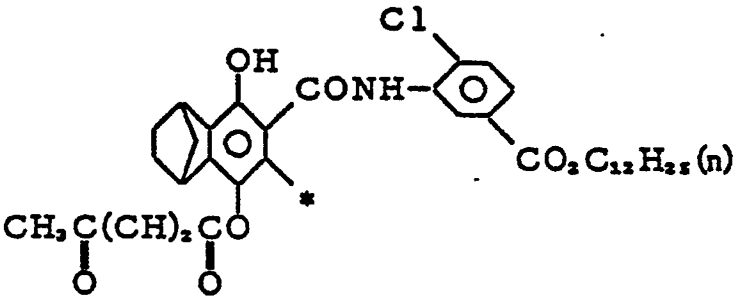

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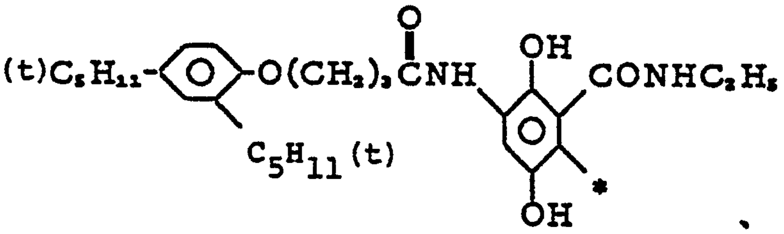

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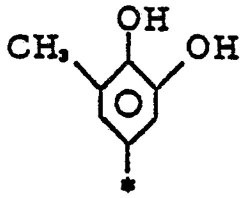

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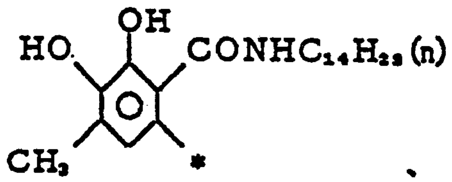

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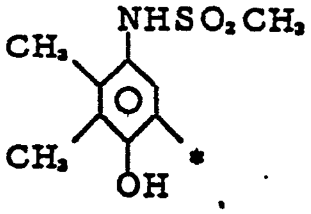

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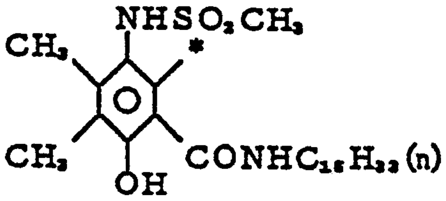

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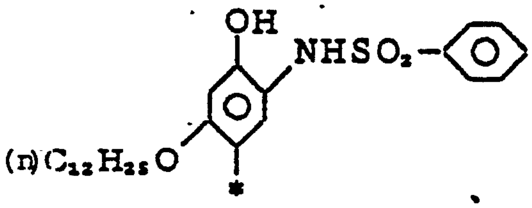

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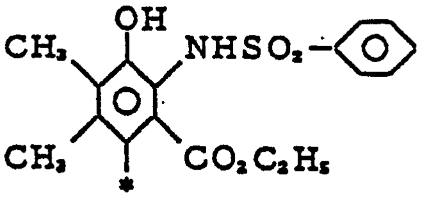

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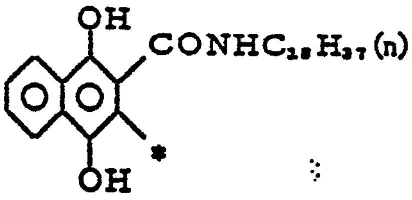

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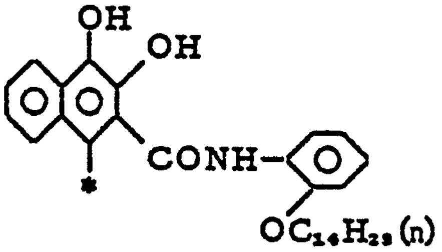

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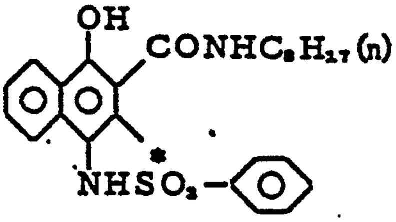

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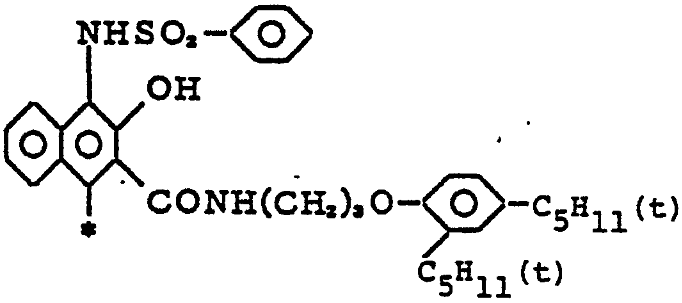

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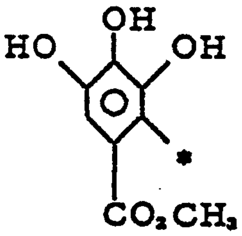

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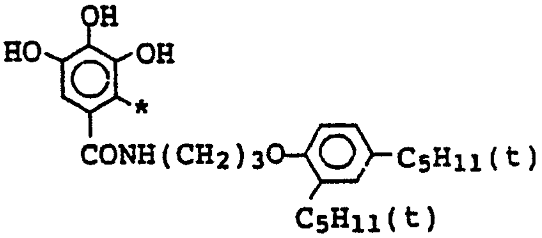
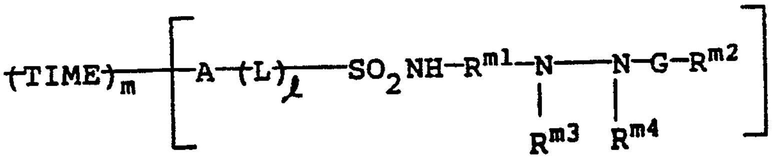


FR means the group -(TIME)$_m$-M$'$, and is preferably a group capable of releasing a compound of the aforesaid formula (M-1) or (M-2) under alkaline conditions. This group is preferably represented by formula (XXII) in which the moiety parenthesized corresponds to the group M′:

$$-(\mathrm{TIME})_m-\left[\mathrm{A}-(\mathrm{L})_\ell-\mathrm{Q}'\right] \qquad \text{(XXII)}$$

or



$$-(\mathrm{TIME})_m-\left[\mathrm{A}-(\mathrm{L})_\ell-\mathrm{SO_2NH}-\mathrm{R}^{m1}-\underset{\substack{|\\ \mathrm{R}^{m3}}}{\mathrm{N}}-\underset{\substack{|\\ \mathrm{R}^{m4}}}{\mathrm{N}}-\mathrm{G}-\mathrm{R}^{m2}\right] \qquad \text{(XXIII)}$$

where A, L, Q′, ℓ, R^{m1}, R^{m2}, R^{m3}, R^{m4} and G are each as defined in (M-1) and (M-2).

In formulae [Ia] to [XXIII], the substituent for each R^{21}, R^{22}, R^{31}, R^{32}, R^{41}, R^{42}, R^{51}, R^{52}, R^{53}, R^{54}, R^{55} R^{56}, R^{57}, R^{8}, R^{m1}, R^{m2}, R^{m3}, R^{m4} has from 0 to 30 carbon atoms and may be further substituted by a substituent, and includes the same as is disclosed in formula [M-2].

Preferable substituent of them includes an alkyl group, an aryl group, an alkoxy group, an acylamino group, a sulfonylamino group, a ureido group, a sulfamoyl group, a carbamoyl group, an alkylthio group, a hydroxy group, a halogen atom, a cyano group, a sulfonyl group, an alkoxy carbonyl group, etc.

More preferable substituent of them includes an alkyl group, an alkoxy group, an acylamino group, a sulfonylamino group, a ureido group, an alkylthio group, a halogen atom, a cyano group, an alkoxy carbonyl group, etc. monovalent organic group, and plural R_{57} groups may be the same or different.

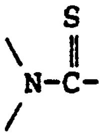
In the formulae (XXII) and (XXIII), TIME represents a timing group capable of releasing the compound of formula (M-1) or (M-2) after release of the group FR; and ℓ and m each is 0 or 1.

As the timing group for TIME, there may be mentioned the groups described in U.S. Patent 4,248,962 and JP-A-57-56837 which release the group M′ by intramolecular substitution reaction after being released from Cp or RED by a coupling reaction or redox reaction; the groups described in British Patent 2,072,363A, JP-A-57-154234, JP-A-57-188035, JP-A-56-114946, JP-A-57-56837, JP-A-58-209736, JP-A-58-209737, JP-A-58-209738, JP-A-58-209740 and JP-A-58-98728, which release the group M′ by electron transfer via a conjugated system; and the coupling components described in JP-A-57-111536, which release the group M′ by a coupling reaction with the oxidation product of an aromatic primary amine developing agent. The reaction for the timing groups TIME may be either a one-step reaction or a multi-step reaction.

In addition, a trivalent group TIME which is bonded to the coupling position and the non-coupling position and to the group M′ is also preferred as mentioned above. One embodiment which is introduced into a yellow coupler is described in JP-A-58-209740.

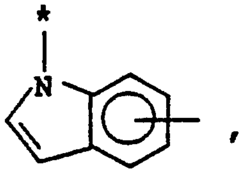
In the group M′, A may be bonded directly to the carbon atom at the coupling position, or any other group than A may be bonded to the coupling carbon atom provided that it is released by a coupling reaction. Preferable examples of A are disclosed, for example, in US Patent 4,719,174. In addition, 2-equivalent releasing group may exist between the coupling carbon atom and the group A. The 2-equivalent releasing group includes for example, an alkoxy group (e.g., a methoxy group), an aryloxy group (e.g., a phenoxy group), an alkylthio group (e.g., an ethylthio group), an arylthio group (e.g., a phenylthio group), a heterocyclic-oxy group (e.g., a tetrazolyloxy group), a heterocyclic-thio group (e.g., a pyridylthio group), or a heterocyclic group (e.g., a hydantoinyl group, a pyrazolyl group, a triazolyl group, or a benzotriazolyl group).

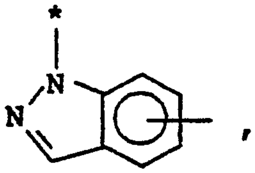
The group A which capable of adsorbing to a silver halide includes, for example, residues of nitrogen-containing hetero-rings having a dissociatable hydrogen atom (e.g., pyrroles, imidazoles, pyrazoles, triazoles, tetrazoles, benzimidazoles, benzopyrazoles, benzotriazoles, uracils, tetrazaindenes, imidazotetrazoles, pyrazolotriazoles and pentazaindenes), hetero-rings having at least one nitrogen atom and other hetero atom(s) (e.g., an oxygen atom, sulfur atom and selenium atom) in the ring (e.g., oxazoles, thiazoles, thiazolines, thiazolidines, thiadiazoles, benzothiazoles, benzoxazoles and benzoselenazoles), mercapto group-containing hetero-rings (e.g., 2-mercaptobenzothiazoles, 2-mercaptopyrimidines, 2-mercaptobenzoxazoles, 1-phenyl-5-mercaptotetrazoles and 5-mercapto-1,3,4-thiadiazoles), thiophenols, alkylthiols (e.g., cysteine), and compounds containing the structure

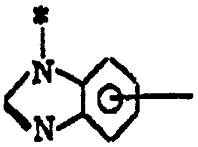


(e.g., thioureas, dithiocarbamates, thioamides, rhodanines, thiazolidinethiones, thiohydantoins and thiobarbituric acids).

Specific examples of the group A are described below, in which * indicates the position bonded to --(TIME)$_m$-.



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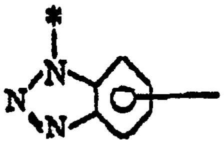
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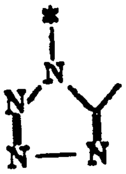
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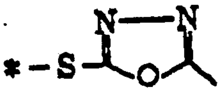
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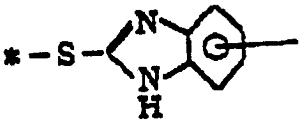
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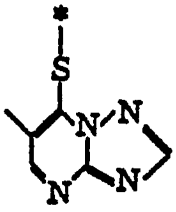
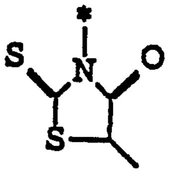


,

$$*-NH\overset{S}{\overset{\|}{C}}NH- ,$$

$$-NH\overset{S}{\overset{\|}{C}}S-* ,$$



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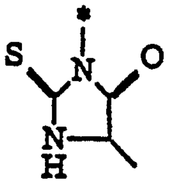
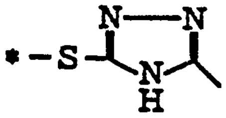


,

$$-CH_2\overset{S}{\overset{\|}{C}}NH-* ,$$



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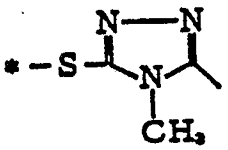
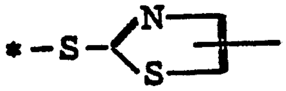

* —S
N
N
N
CH₃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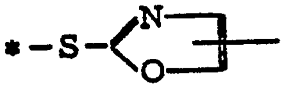
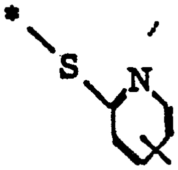
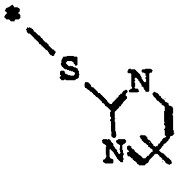
N
S


* —S
N
O


*
S
N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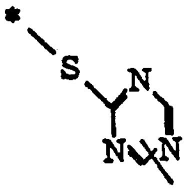
N
N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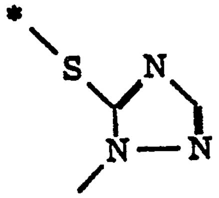
S
N
N
N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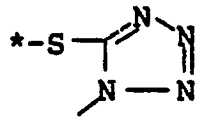
N
N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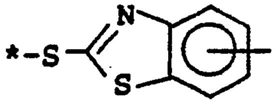
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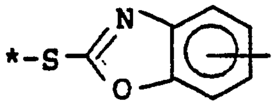
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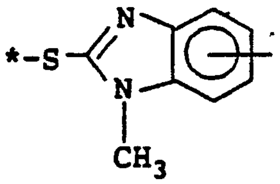
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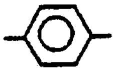
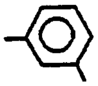
In formulae (M-1) and (M-2), L represents a divalent linking group; and ℓ and n each is 0 or 1.

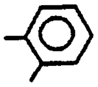
Examples of L include an alkylene group, an alkenylene group, an arylene group, a divalent heterocyclic group, -O-, -S-, an imino group, -COO-, -CONH-, -NHCONH-, -NHCOO-, $-SO_2NH-$, -CO-, $-SO_2-$, -SO-, $-NHSO_2NH-$ or a combination of two or more of these groups.

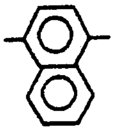
When one of the divalent linking groups for L is properly selected from groups which may be released by the action of components in a developer (e.g., hydroxide ion, hydroxylamine, sulfite ion, etc.), it is possible to control the fogging capacity of the foggant-releasing compound or to deactivate the same. For example, when L group which dissociates in alkaline solution during processing is used, a lowering of fogging occurred in the latter period is attained. Preferable examples of L are disclosed in US Patent 4,719,174.

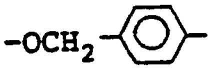
$-CH_2-$,
$-CH_2CH_2-$,
$-OCH_2-$,
$-OCH_2CH_2-$,
$-SCH_2-$,
-COO-,

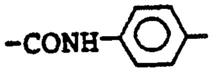
 ,

 ,

 ,

 ,


-OCH2
 ,


-CONH
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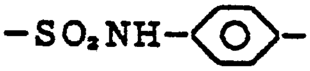
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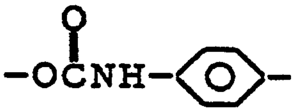
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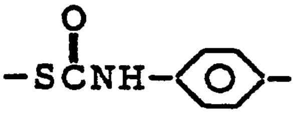
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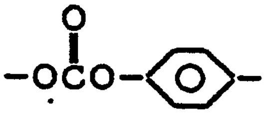
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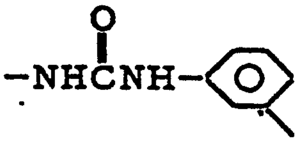
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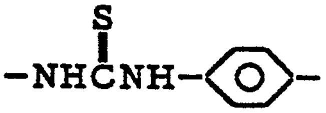
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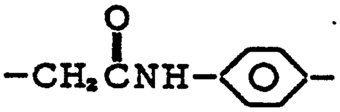
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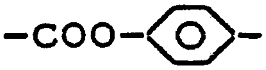
—COO—

,


CONH—

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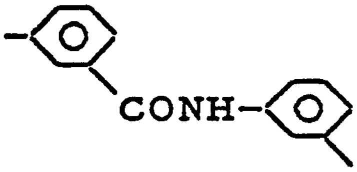
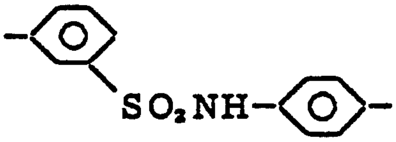

CONH—

,


SO₂NH—

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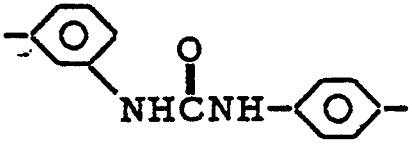
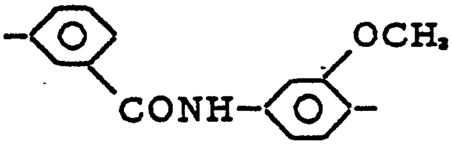
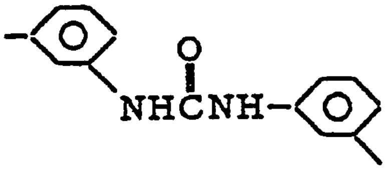

O
NHCNH—

,


OCH₃
CONH—

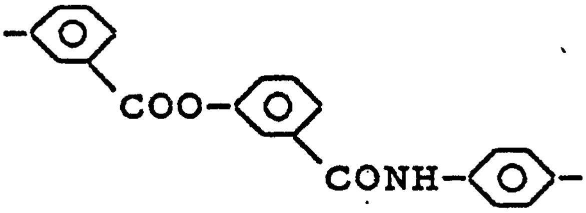
,


O
NHCNH—

,


—OCH₂CONH—

,



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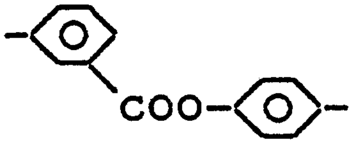

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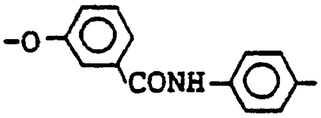

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The group (Q) is now described in greater detail. The heterocyclic ring formed by Z includes, for example, quinolinium, benzothiazolium, benzimidazolium pyridinium, thiazolinium, thiazolium, naphthothiazolium, selenazolium, benzoselenazolium, imidazolium, tetrazolium, indolenium, pyrrolinium, acridinium, phenanthridium, isoquinolinium, oxazolium, naphthoxazolium and benzoxazolium nuclei. The group Z may be substituted, and the substituents therefore include, for example, an alkyl group, an alkenyl group, an aralkyl group, an aryl group, an alkynyl group, a hydroxyl group, an alkoxy group, an aryloxy group, a halogen, an amino group, an alkylthio group, an arylthio group, an acyloxy group, an acylamino group, a sulfonyl group, a sulfonyloxy group, a sulfonylamino group, a carboxyl group, an acyl group, a carbamoyl group, a sulfamoyl group, a sulfo group, a cyano group, a ureido group, a urethane group, a carbonate group, a hydrazine group, a hydrazone group, and an imino group. Z may be substituted by at least one substituent selected from the above-menthoned substi tuents, and when Z is substituted by two or more substituents, the plural substituents may be same or different. In addition, the substituents may further be substituted by any other substituents, for example, those mentioned above.

Other substituents for Z include a heterocyclic quaternary ammonium group formed by Z via the linking group L. In this case, the formula (Q) forms a dimer structure.

Preferred heterocyclic rings formed by Z include quinolinium, benzothiazolium, benzimidazolium, pyridinium, acridinium, phenanthridium and isoquinolinium nuclei. More preferably, the rings are quinolinium, benzothiazolium and benzimidazolium nuclei, and especially preferably they are quinolinium and benzothiazolium nuclei. Most preferably the ring is a quinolinium nucleus.

The aliphatic group represented by R^1 and R^2 may be an unsubstituted alkyl group having from 1 to 18 carbon atoms or a substituted alkyl group in which the alkyl moiety has from 1 to 18 carbon atoms. As substituents for the alkyl group, those mentioned for Z above are included.

The aromatic group represented by R^2 has from 6 to 20 carbon atoms, which may be, for example, a phenyl group or a naphthyl group. The group may optionally be substituted, and as substituents for the aromatic group, those mentioned for Z above are included.

At least one of R^1, R^2 and Z contains an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or R^1 and R^2 form a 6-membered ring to complete a dihydropyridinium nucleus. These may also be substituted, and as substituents for the groups, those mentioned for Z above are included.

The hydrazine group is especially preferably substituted by an acyl group or a sulfonyl group.

The hydrazone group is especially preferably substituted by an aliphatic group or an aromatic group.

The acyl group is preferably a formyl group or an aliphatic or aromatic ketone residue.

Regarding the alkynyl group for at least one of R^1, R^2 and Z, the alkynyl group preferably has from 2 to 18 carbon atoms, which includes, for example, an ethynyl group, as propargyl group, a 2-butynyl group, a 1-methylpropargyl group, a 1,1-dimethylpropargyl group, a 3-butynyl group, an a 4-pentynyl group.

The alkynyl group may be substituted, and as the substituents for the group, those mentioned for Z above are included. For example, there may be mentioned a 3- phenylpropargyl group, a 3-methoxycarbonylpropargyl group and a 4-methoxy-2-butynyl group.

At least one substituent on the group or ring represented by R^1, R^2 or Z is preferably an alkynyl group or an acyl group, an it is also preferred that R^1 and R^2 are linked to form a dihydropyridinium skeleton. Most preferably, at least one alkynyl group is substituted on the group or ring represented by R^1, R^2 or Z.

Especially preferably, R^2 is a propargyl group.

Preferable substituent of substituents for R^1, R^2 and Z includes an alkyl group, an alkenyl group, an aryl group, an alkynyl group, an alkoxy group, an aryloxy group, a halogen atom, a sulfonyl group, a sulfonylamino group, an acyl group, a carbamoyl group, an acylamino group, a ureido group, etc.

More preferable substituent of them includes an alkyl group, an alkenyl group, an alkynyl group, a sulfonylamino group, an acylamino group, a ureido group, an alkoxy group, etc.

The counter ion Y for charge balance may be any anion to neutralize the positive charge caused by the quaternary ammonium salt in the heterocyclic ring, and it may be a bromide ion, chloride ion, iodide ion, p-toluenesulfonate ion, ethylsulfonate ion, perchlorate ion, trifluoromethanesulfonate ion or thiocyanate ion. In this case, n is 1. When the heterocyclic quaternary ammonium salt in the formula contains an anion substituent such as a sulfoalkyl substituent, the salt may be in the form of a betain. In this case, no pair ion is necessary and n is 0. When the heterocyclic quaternary ammonium salt has two anion substituents such as two sulfoalkyl groups, Y is a cationic pair ion, which may be, for example, an alkali metal ion (e.g., a sodium ion, a potassium ion), or an ammonium ion (e.g., a triethylammonium ion).

R^{m1} represents an aromatic group, for example, a phenylene group or a naphthylene group.

R^{m1} may be substituted by at least one substituent, including the following groups which may further be substituted: an alkyl group, an aralkyl group, an alkoxy group, an alkyl- or aryl-substituted amino group, an acylamino group, a sulfonylamino group, a ureido group, a urethane group, an aryloxy group, a sulfamoyl group, a carbamyl group, an aryl group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfinyl group, a hydroxyl group, a halogen atom, a cyano group, a sulfo group, an alkenyl group, an amino group, a sulfo group, an alkynyl group, an acyloxy group, an alkoxy carbonyl group, and a carboxyl group. These groups may be bonded to each other to form a ring, if desired.

R^{m1} is preferably a phenylene group, and especially preferably it is a 1,2-phenylene group.

When G represents a carbonyl group, R^{m2} is preferably a hydrogen atom, an alkyl group (e.g., a methyl group, a trifluoromethyl group, a 3-hydroxypropyl group, or a 3-methanesulfonamide group, a propyl group), an aralkyl group (e.g., an o-hydroxybenzyl group), an aryl group (e.g., a phenyl group, a 3,5-dichlorophenyl group, an o-methanesulfonamidophenyl group or a 4-methanesulfonylphenyl group), and it is especially preferably a hydrogen atom.

When G is a sulfonyl group, R^{m2} is preferably an alkyl group (e.g., a methyl group), an aralkyl group (e.g., a o-hydroxyphenylmethyl group), an aryl group (e.g., a phenyl group) or a substituted amino group (e.g., a dimethylamino group).

R^{m2} may have at least one substituent, including substituents for R^{m1} above and in addition, an acyl group, an aryl-oxycarbonyl group, or a nitro group.

In addition, the substituents may further be substituted by any other substituents, for example, those mentioned above. If possible, these groups may be bonded to each other to form a ring.

The alkylsulfonyl group for R^{m3} and R^{m4} may have from 1 to 12 carbon atoms, which includes, for example, a methanesulfonyl group, a trifluoromethanesulfonyl group, and a cyclohexanesulfonyl group. The arylsulfonyl group for R^{m3} and R^{m4} may have from 6 to 20 carbon atoms, which includes, for example, a benzenesulfonyl group. The acyl group for R^{m3} and R^{m4} may have from 1 to 12 carbon atoms, which includes, for example, an acetyl group, a trifluoroacetyl group and a p-cyanobenzoyl group.

R^{m3} and R^{m4} each are most preferably a hydrogen atom. G is most preferably a carbonyl group.

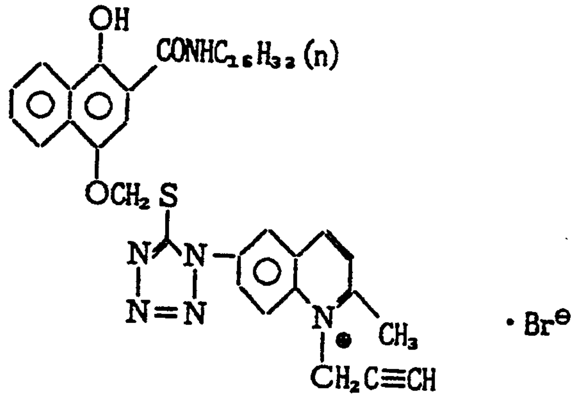
R^{m3} and R^{m4} each may have at least one substituent, including substituents for R^{m2}.

Preferable substituent of R^{m1} to R^{m4} includes an alkyl group, an aryl group, an alkoxy group, an sulfonylamino group, an acylamino group, a ureido group, a urethane group, a hydroxy group, a halogen atom, a cyano group, etc.

More preferable substituent of them includes an alkyl group, an alkoxy group, a sulfonylamino group, a ureido group, an acylamino group, and a hydroxy group, etc.

Specific examples of the compounds for use in the present invention are described below, but the present invention is not to be construed as being limited thereto.

(1-1)



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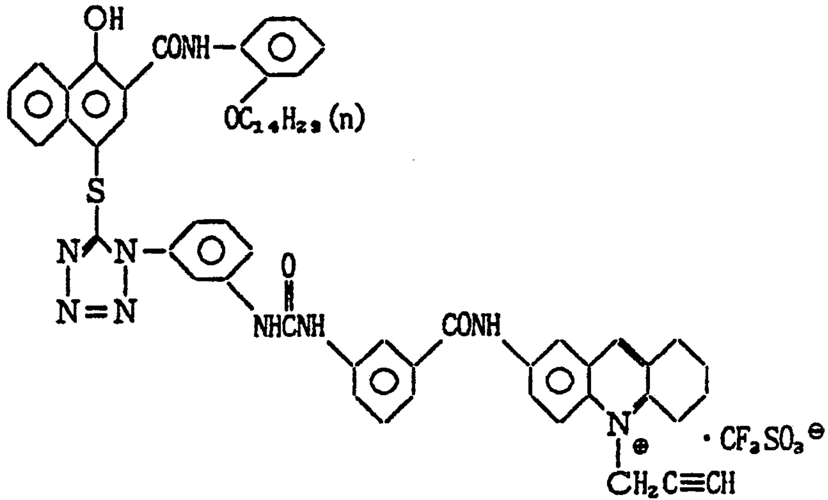
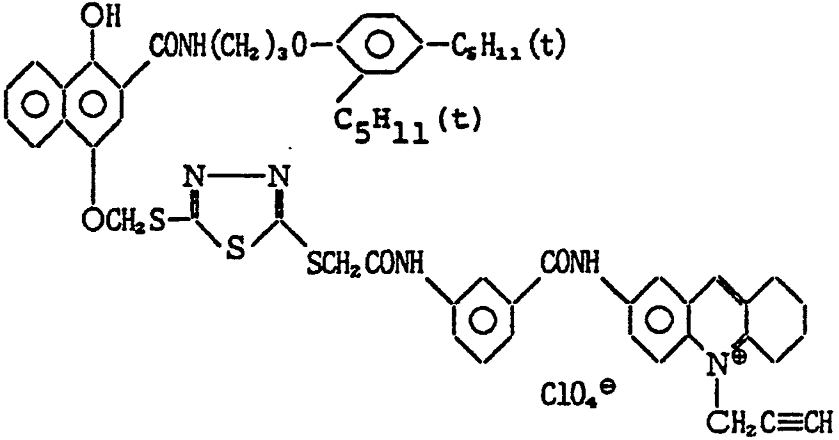
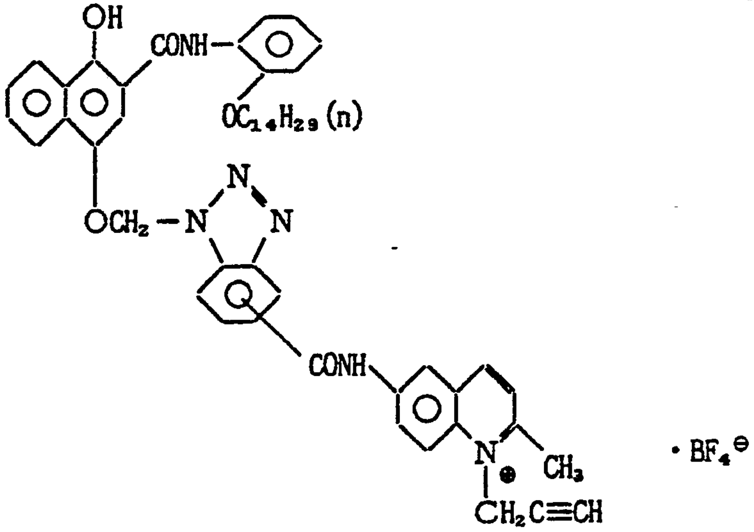

OH
CONH
OC₁₄H₂₉(n)
S
N
N
N=N
O
NHCNH
CONH
N⊕
CH₂C≡CH
· CF₃SO₃⊖

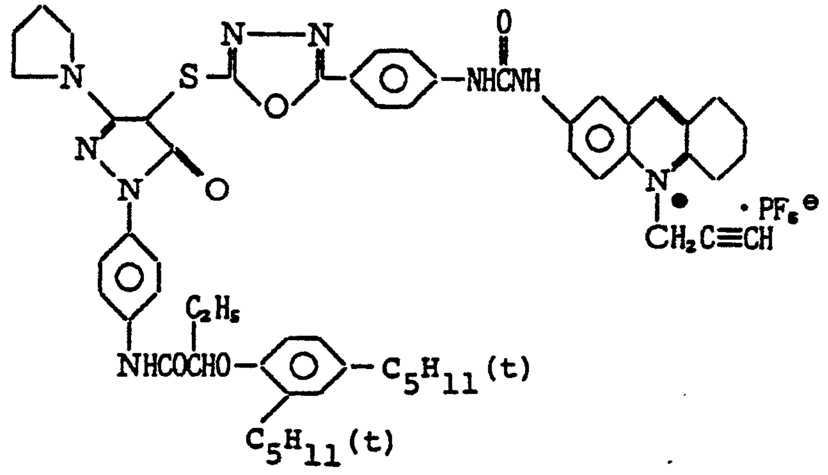
〔1-3〕


OH
CONH(CH₂)₃O
C₅H₁₁(t)
C₅H₁₁(t)
N—N
OCH₂S
S
SCH₂CONH
CONH
N⊕
ClO₄⊖
CH₂C≡CH

〔1-4〕


OH
CONH
OC₁₄H₂₉(n)
N
OCH₂—N
N
CONH
N⊕
CH₃
CH₂C≡CH
· BF₄⊖

[1-5]



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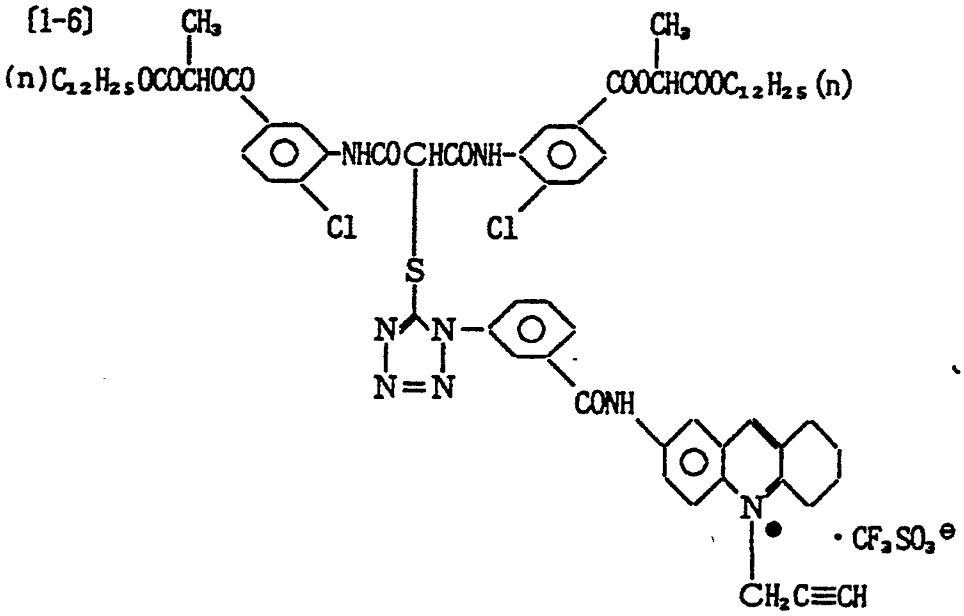

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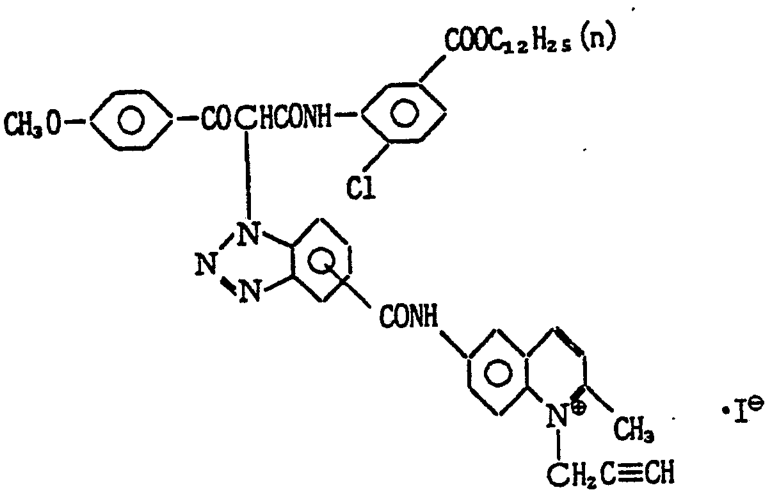

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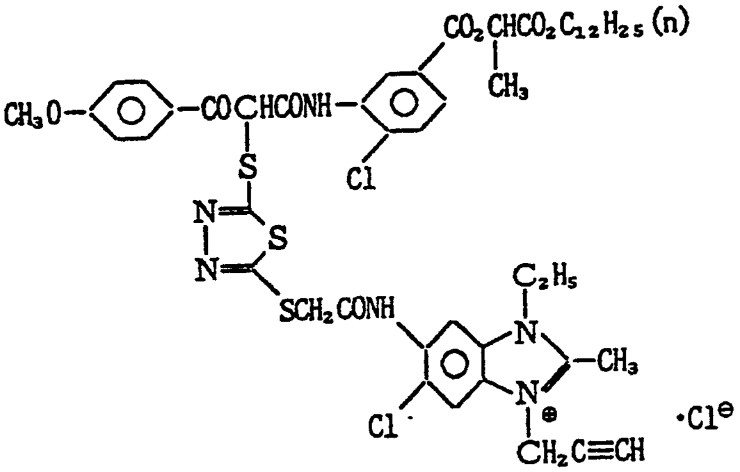

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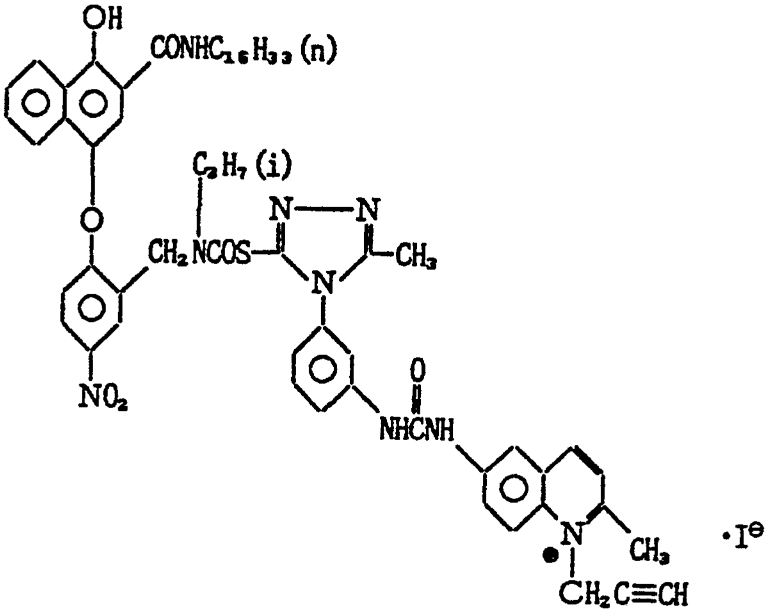

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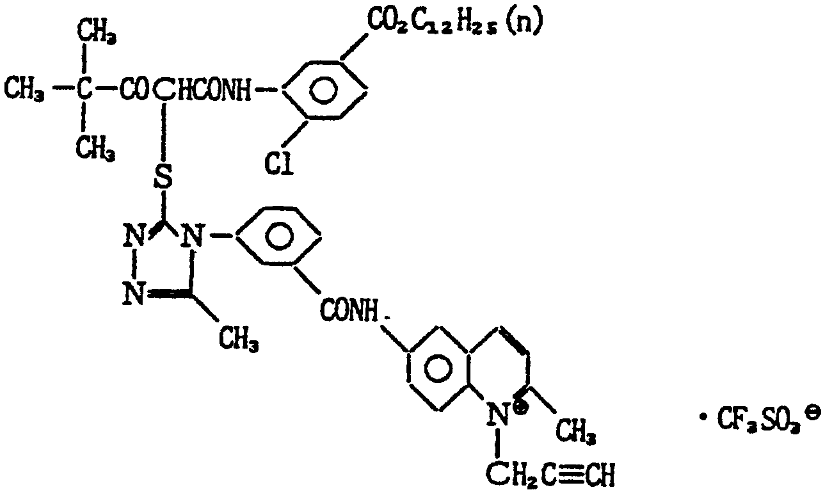

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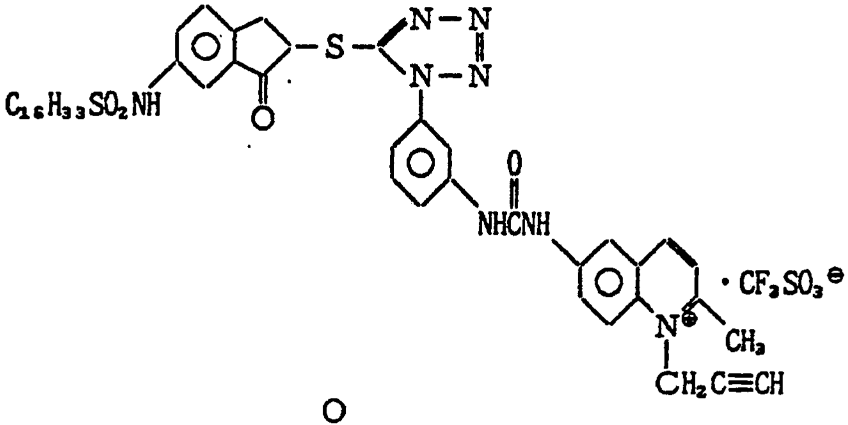

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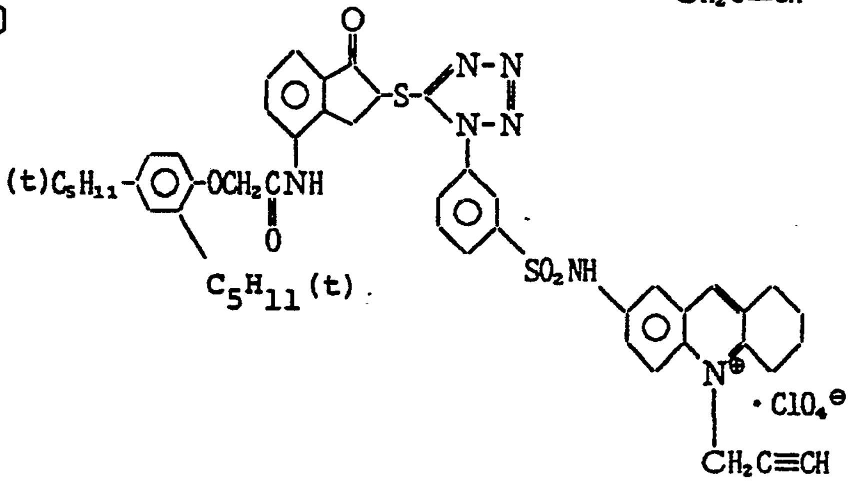

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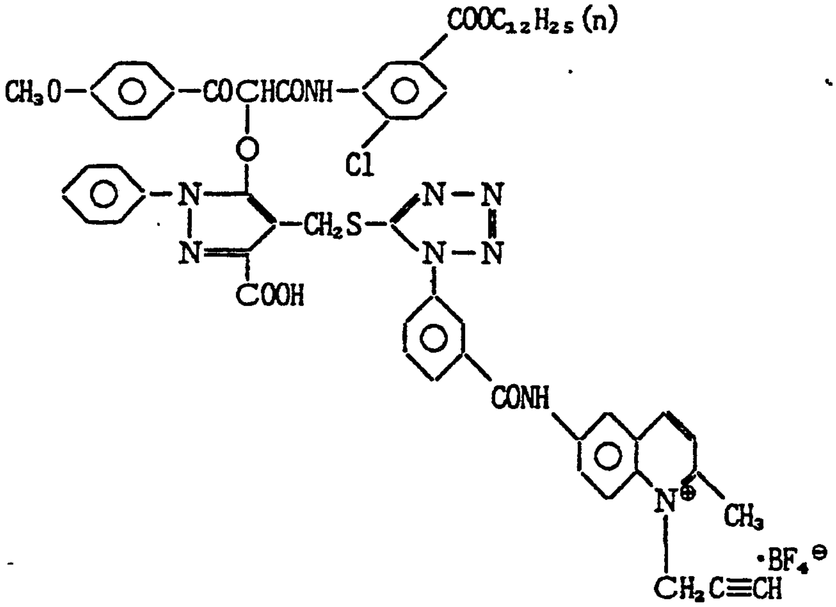
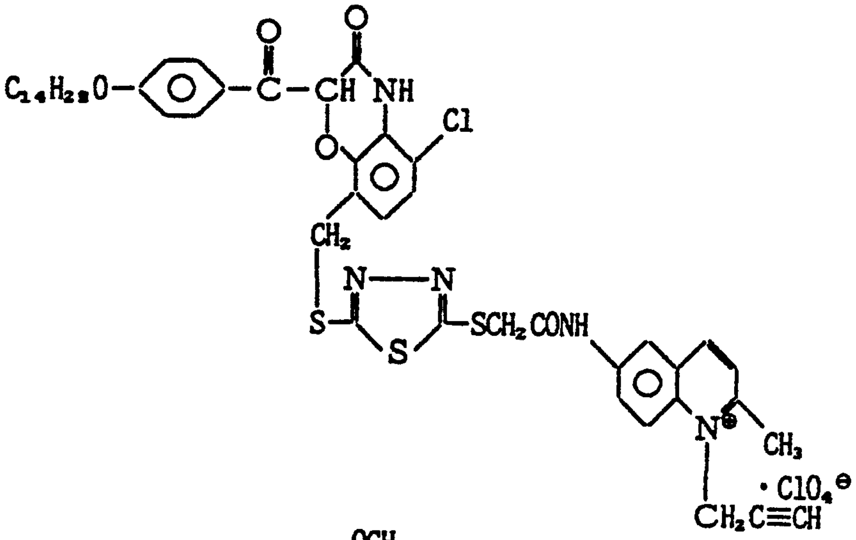
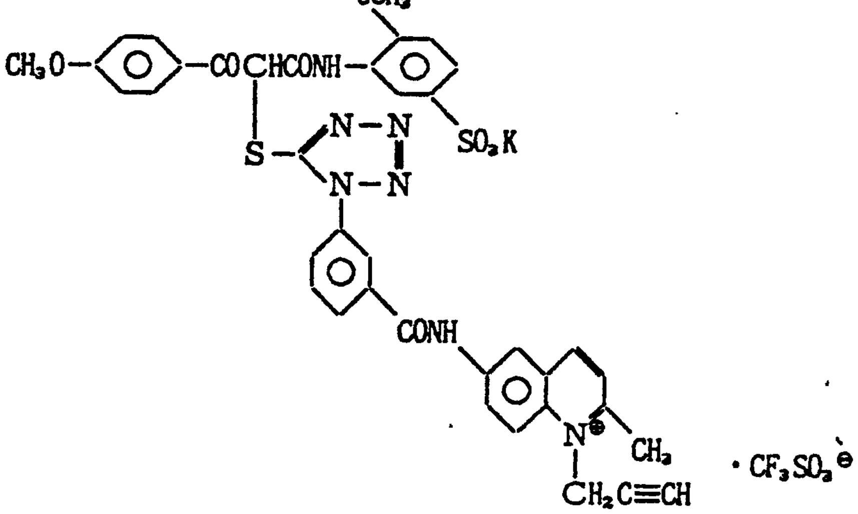


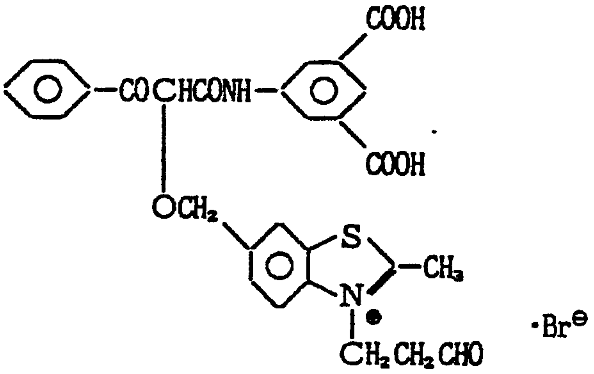
(1-14)



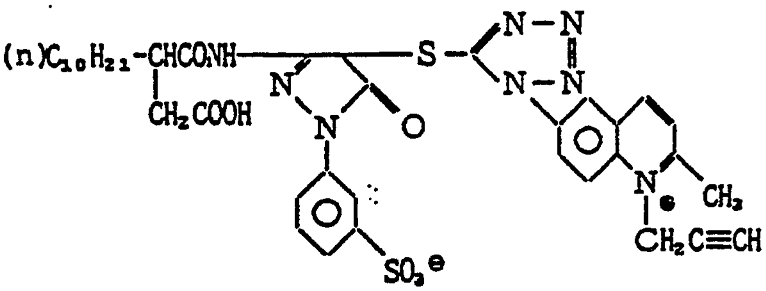
(1-15)



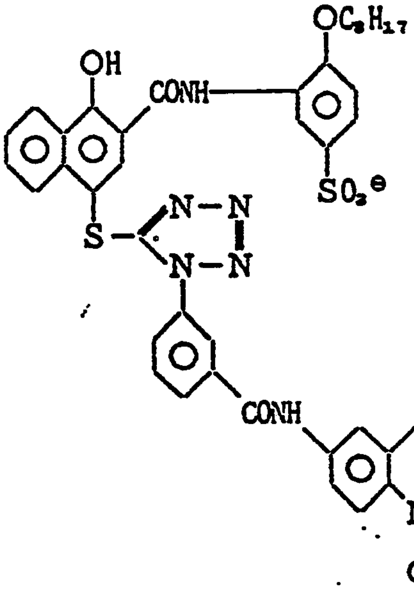
(1-16)



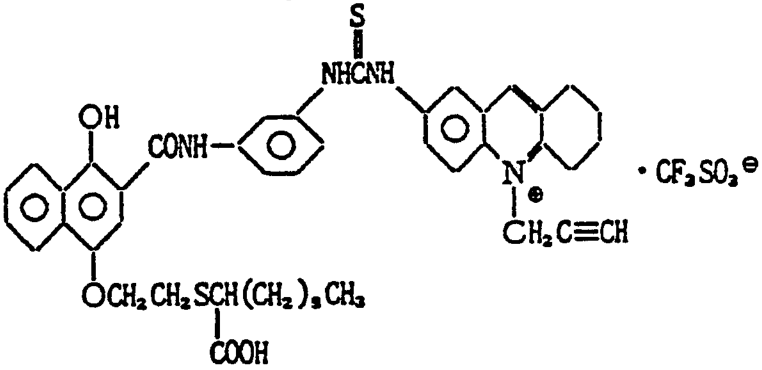
(1-17)



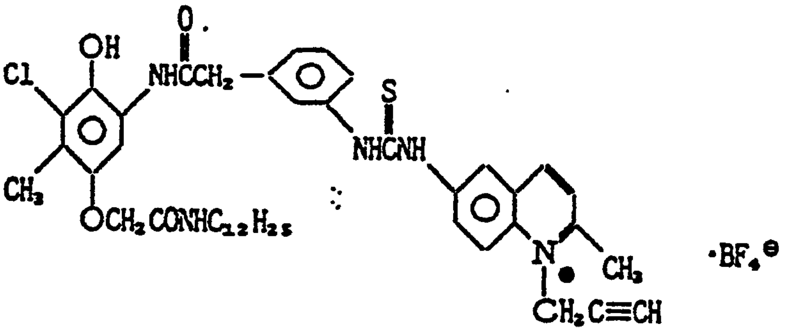
(1-18)



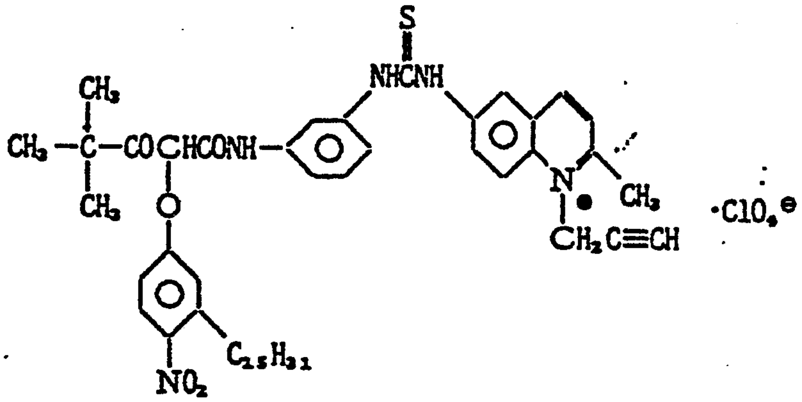
(2-1)



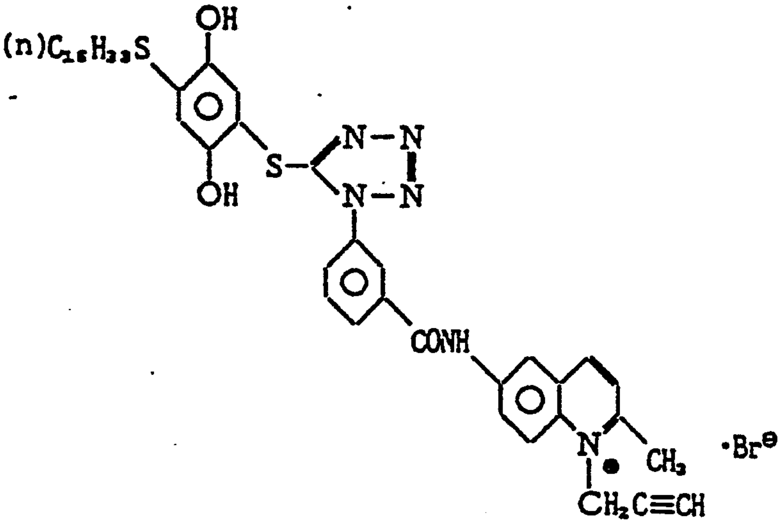
[2-2]


OH
Cl
NHCCH₂
O
S
NHCNH
CH₃
OCH₂CONHC₁₂H₂₅
N
CH₃
CH₂C≡CH
·BF₄⊖

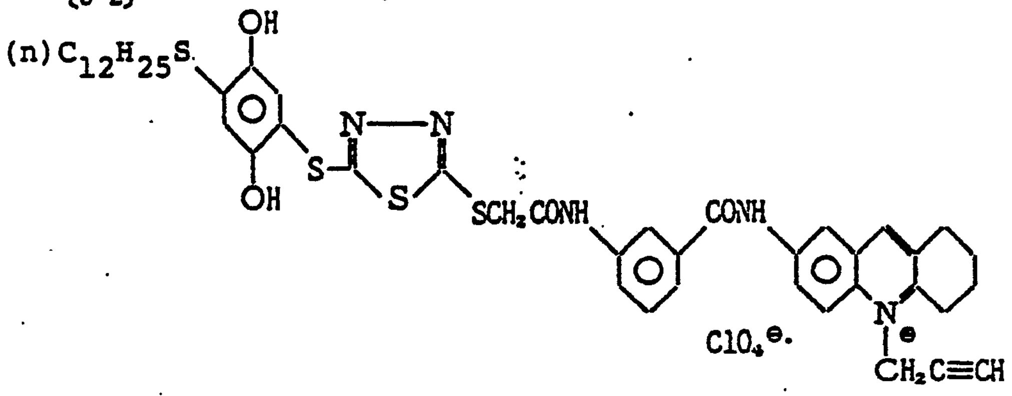
[2-3]


S
NHCNH
CH₃
CH₃—C—COCHCONH—
CH₃
O
N
CH₃
CH₂C≡CH
·ClO₄⊖
C₁₅H₃₁
NO₂

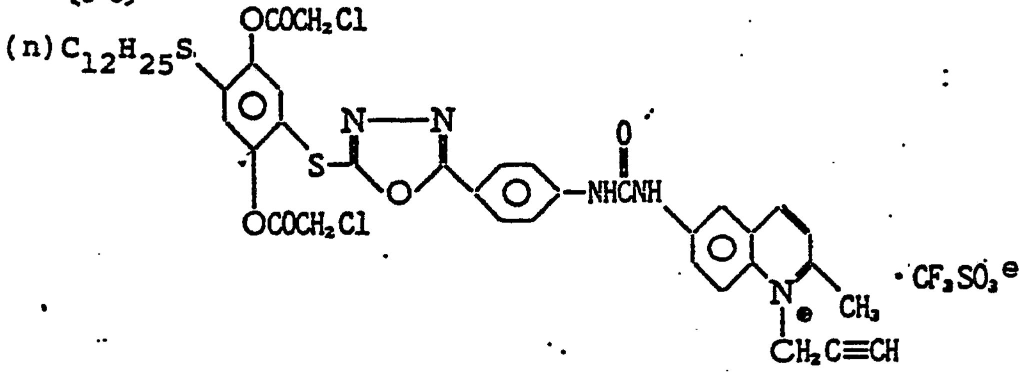
[3-1]


OH
(n)C₁₆H₃₃S
S
N—N
N—N
OH
CONH
N
CH₃
CH₂C≡CH
·Br⊖

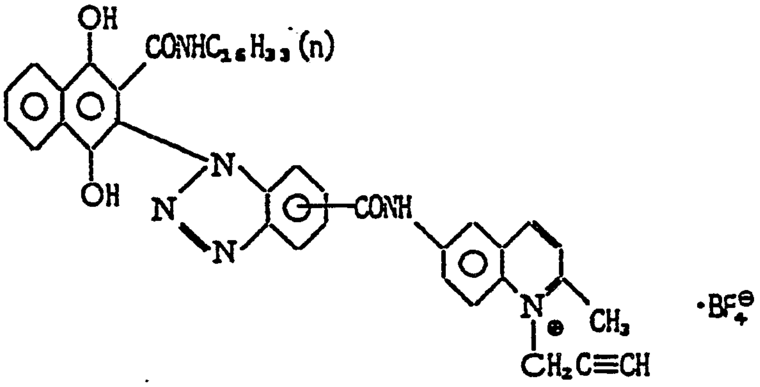
[3-2]


OH
(n)C12H25S
N
N
S
S
OH
SCH2CONH
CONH
ClO4⊖·
N⊕
CH2C≡CH

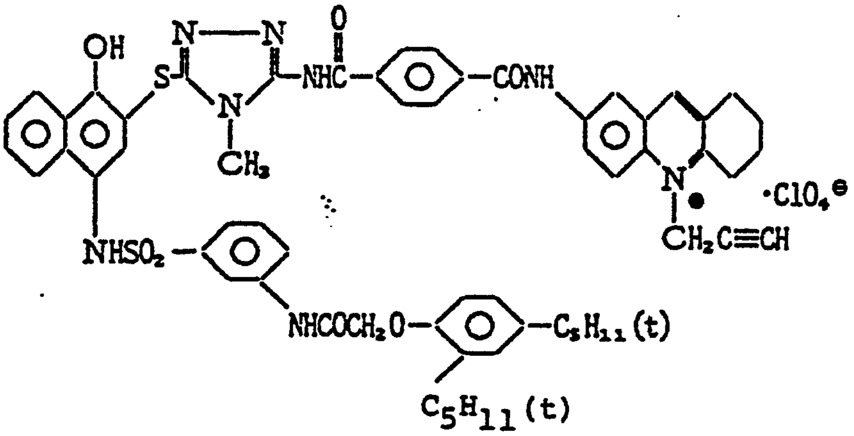
[3-3]


OCOCH2Cl
(n)C12H25S
N
N
S
O
O
NHCNH
OCOCH2Cl
·CF3SO3⊖
N⊕
CH3
CH2C≡CH

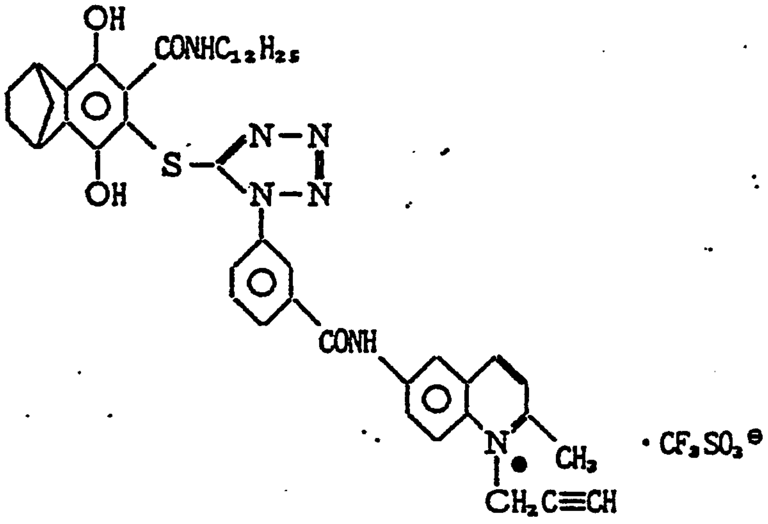
[3-4]


OH
CONHC16H33(n)
N
N
N
OH
CONH
N⊕
CH3
·BF4⊖
CH2C≡CH

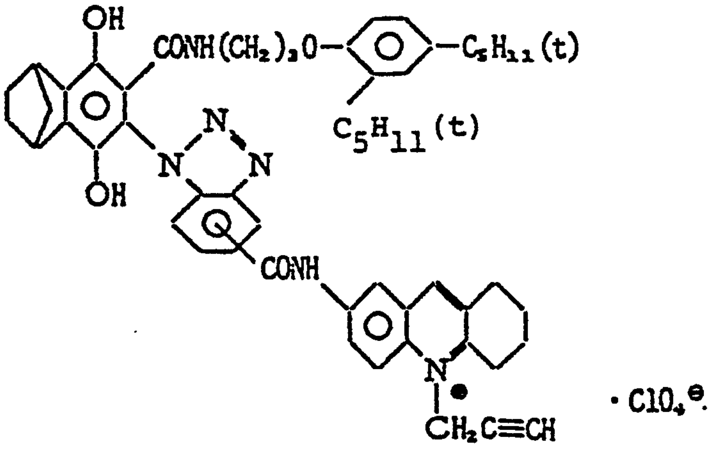
(3-5)


OH
N—N
O
S
NHC
CONH
N
CH₃
N
·ClO₄⊖
CH₂C≡CH
NHSO₂
NHCOCH₂O
C₅H₁₁(t)
C₅H₁₁(t)

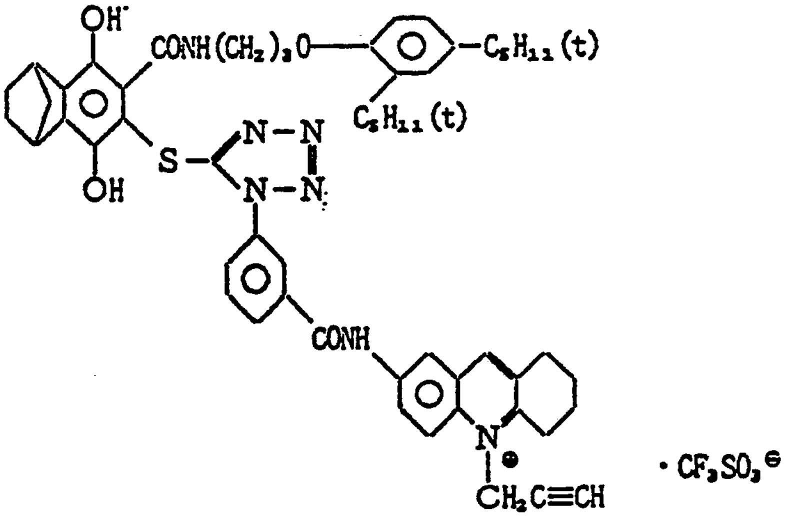
(3-6)


OH
CONHC₁₂H₂₅
N—N
S
N—N
OH
CONH
N
CH₃
·CF₃SO₃⊖
CH₂C≡CH

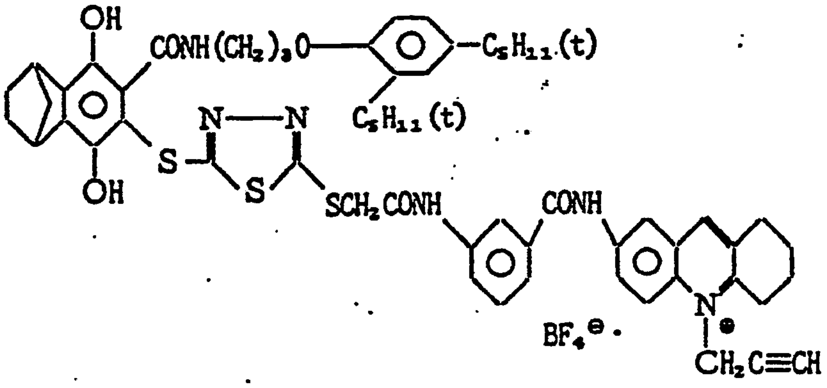
(3-7)


OH
CONH(CH₂)₃O
C₅H₁₁(t)
C₅H₁₁(t)
N
N
N
OH
CONH
N
·ClO₄⊖
CH₂C≡CH

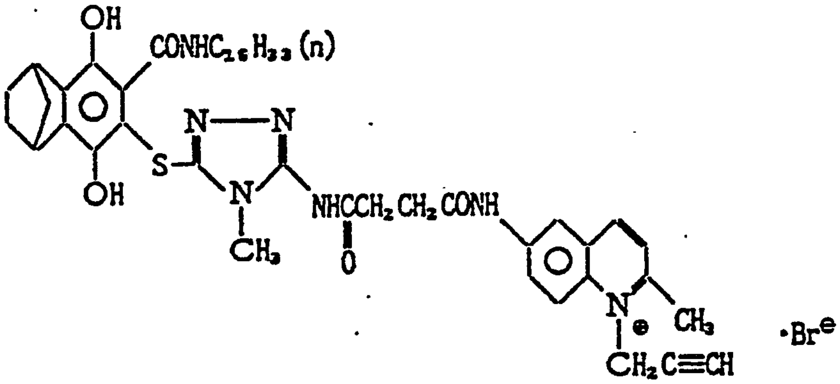
[3-8]



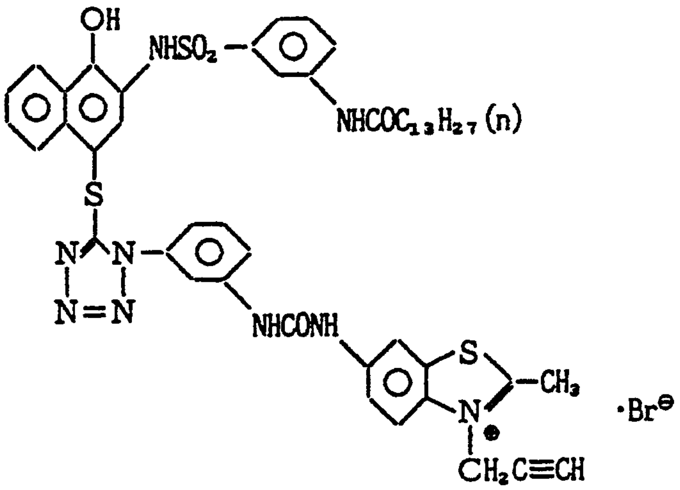
[3-9]



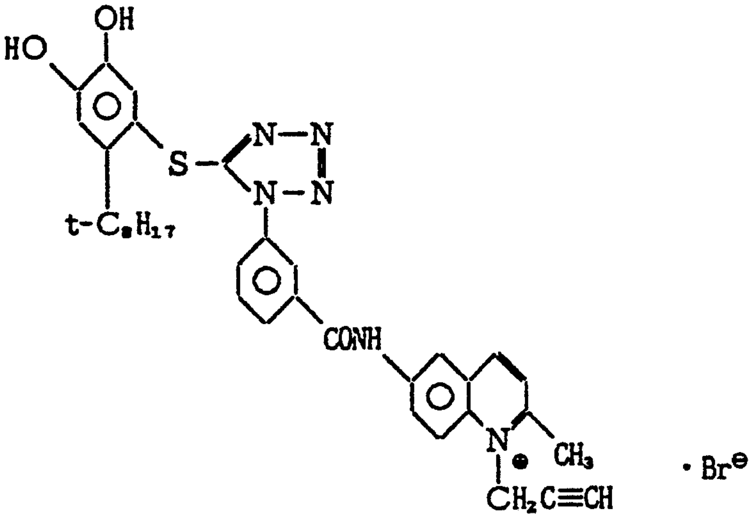
[3-10]



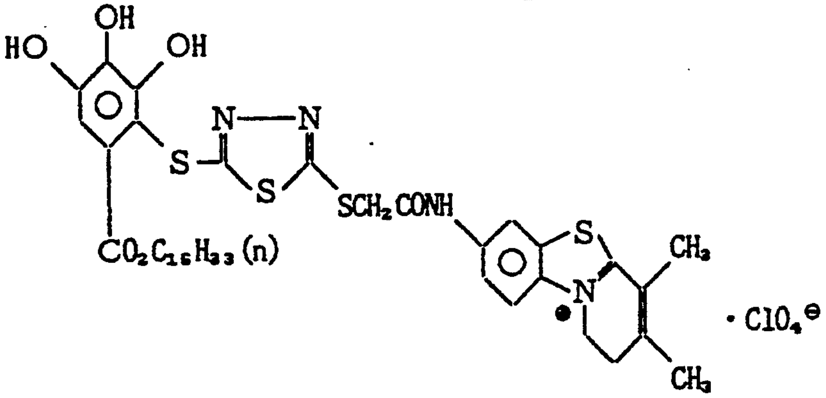
(3-11)



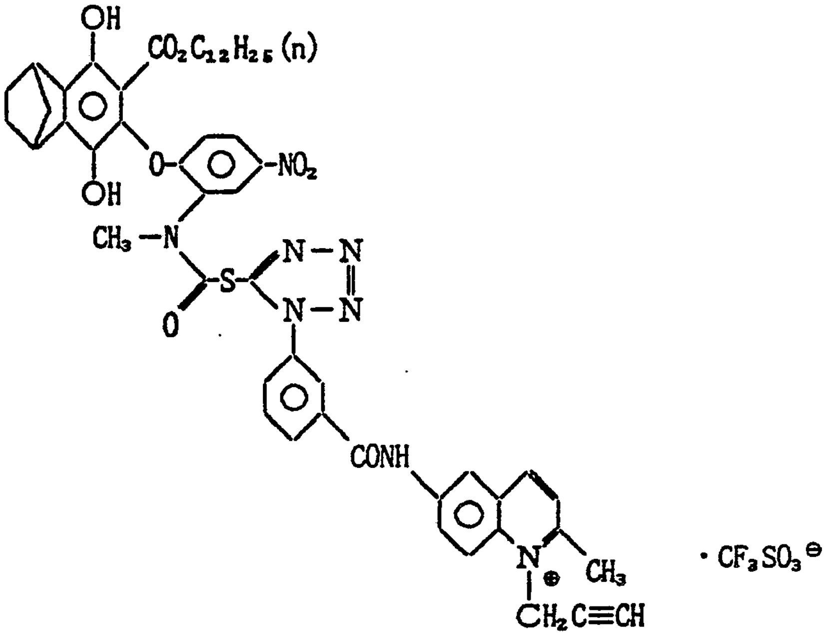
(3-12)



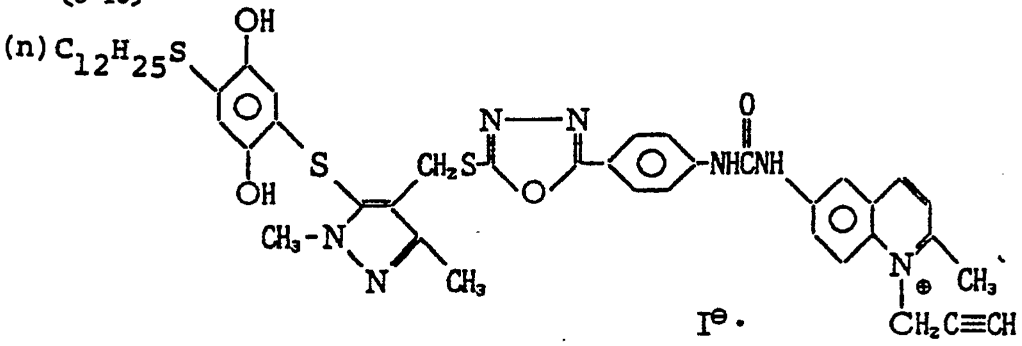
(3-13)



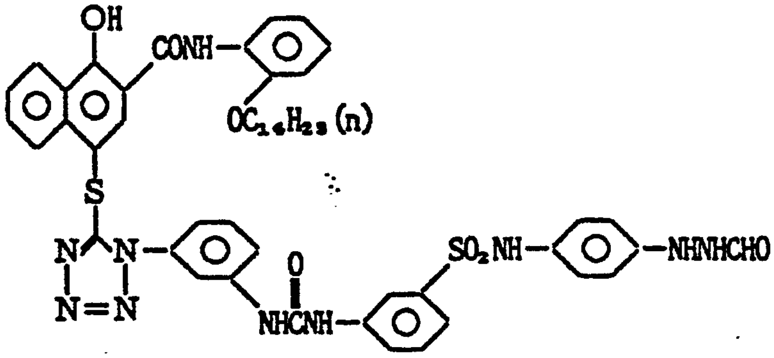
[3-14]



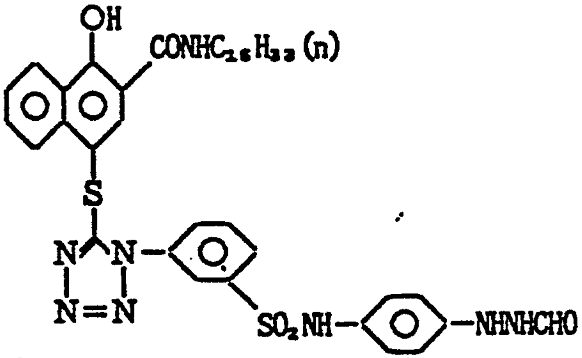
[3-15]



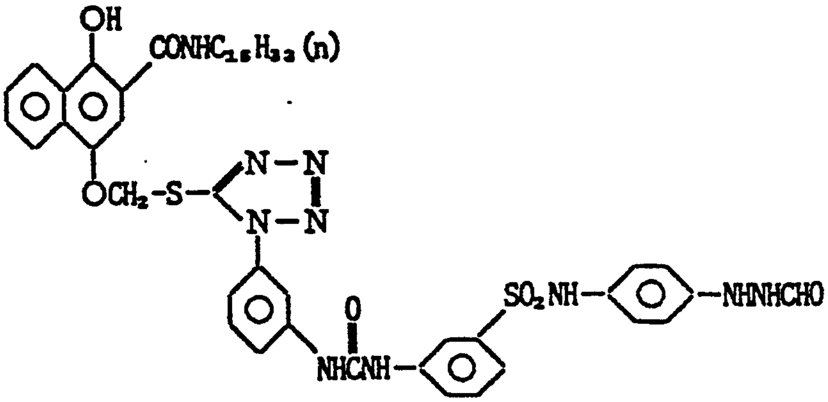
[4-1]


OH
CONH
OC14H29(n)
S
N
N
N=N
O
NHCNH
SO2NH
NHNHCHO

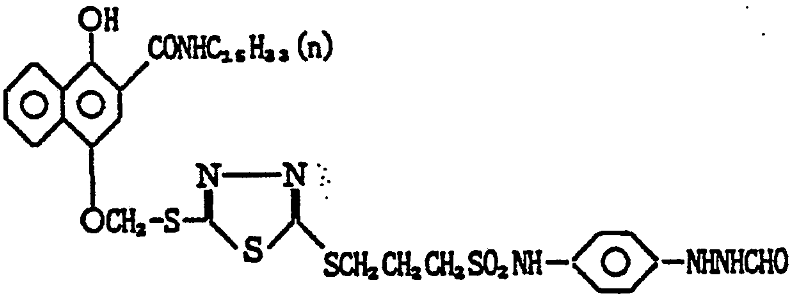
[4-2]


OH
CONHC16H33(n)
S
N
N
N=N
SO2NH
NHNHCHO

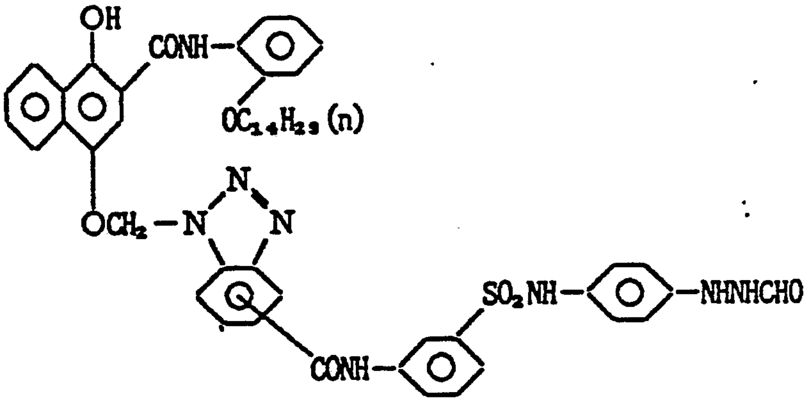
[4-3]


OH
CONHC16H33(n)
OCH2-S
N-N
N-N
O
NHCNH
SO2NH
NHNHCHO

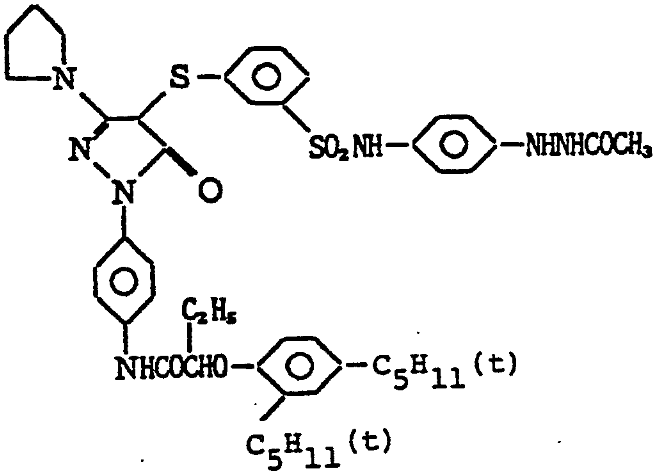
[4-4]


OH
CONHC16H33(n)
N
N
OCH2-S
S
SCH2CH2CH2SO2NH
NHNHCHO

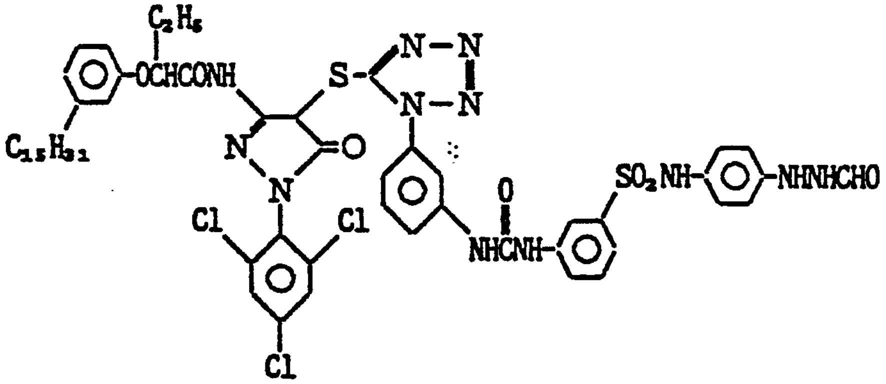
[4-5]


OH
CONH
OC14H29(n)
N
N
OCH2
N
SO2NH
NHNHCHO
CONH

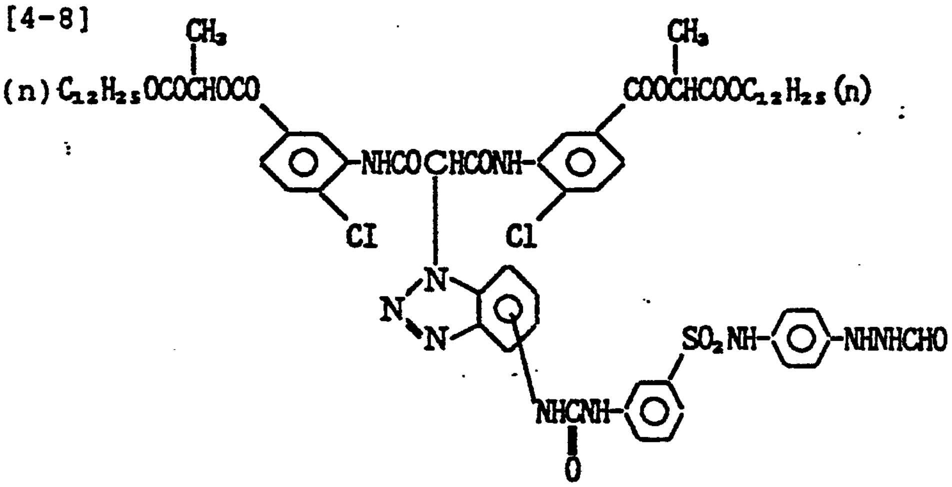
[4-6]


N
S
SO2NH
NHNHCOCH3
N
N
O
C2H5
NHCOCHO
C5H11(t)
C5H11(t)

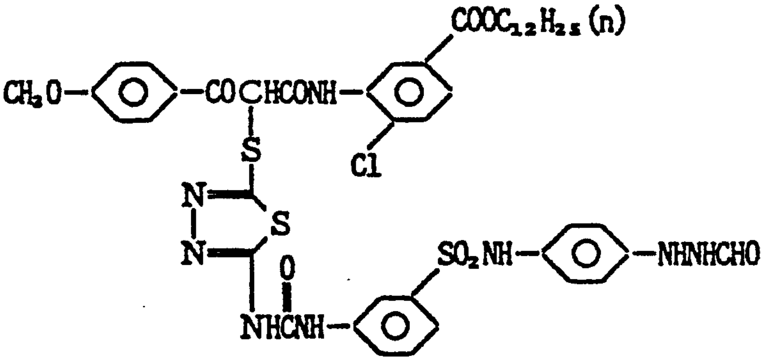
[4-7]


C2H5
OCHCONH
C15H31
S
N
O
Cl
Cl
Cl
SO2NH
NHNHCHO
NHCNH

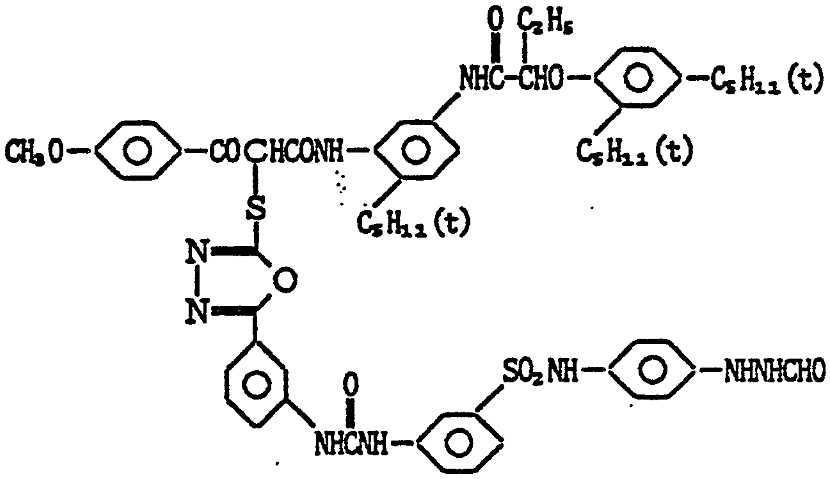
[4-8]


CH3
(n)C12H25OCOCHOCO
CH3
COOCHCOOC12H25(n)
NHCOCHCONH
Cl
Cl
N
SO2NH
NHNHCHO
NHCNH
O

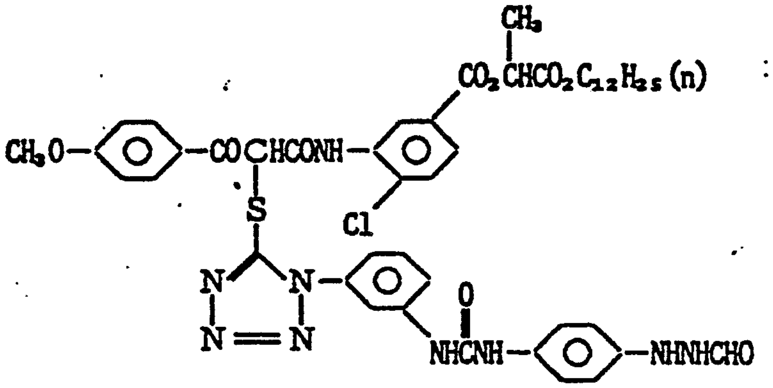
[4-9]


COOC12H25(n)
CH3O
COCHCONH
S
Cl
N
S
SO2NH
NHNHCHO
NHCNH
O

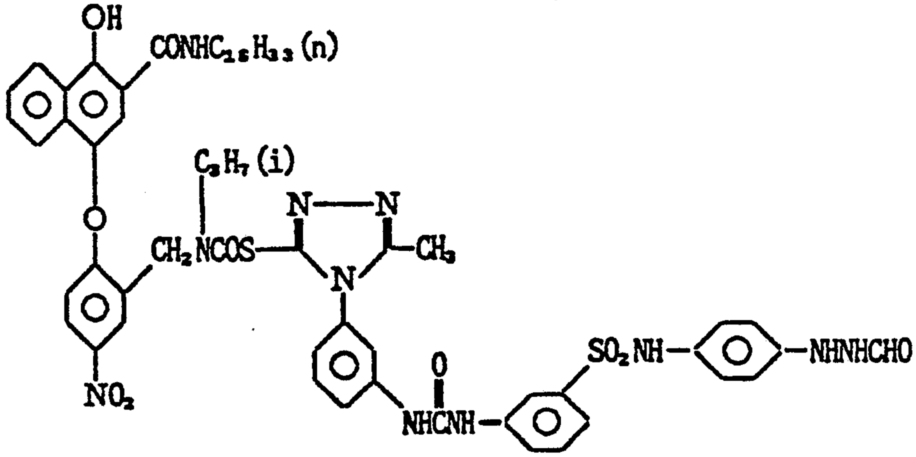
[4-10]



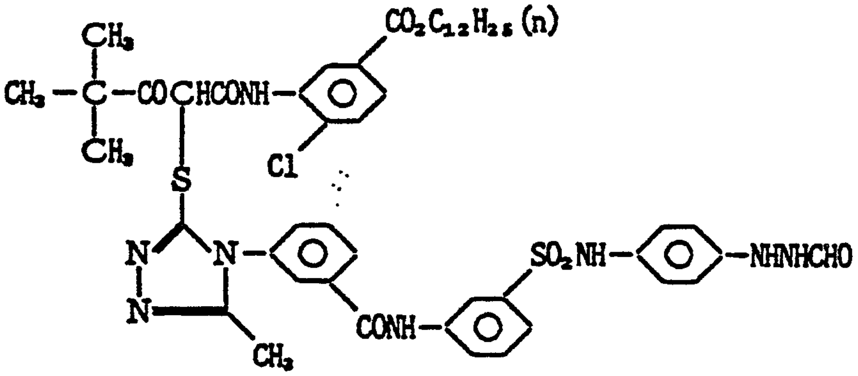
[4-11]



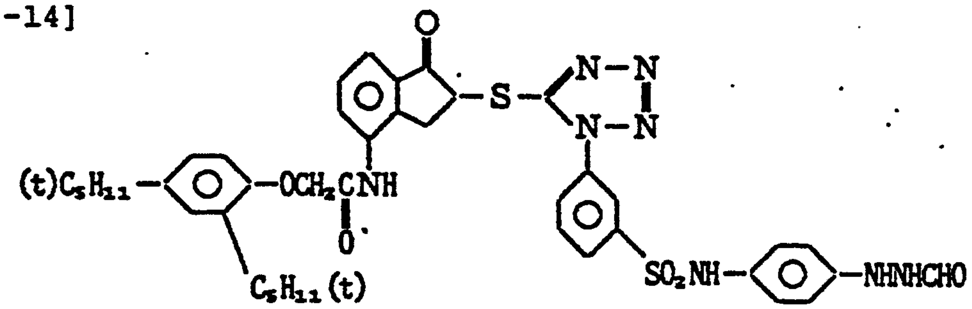
[4-12]



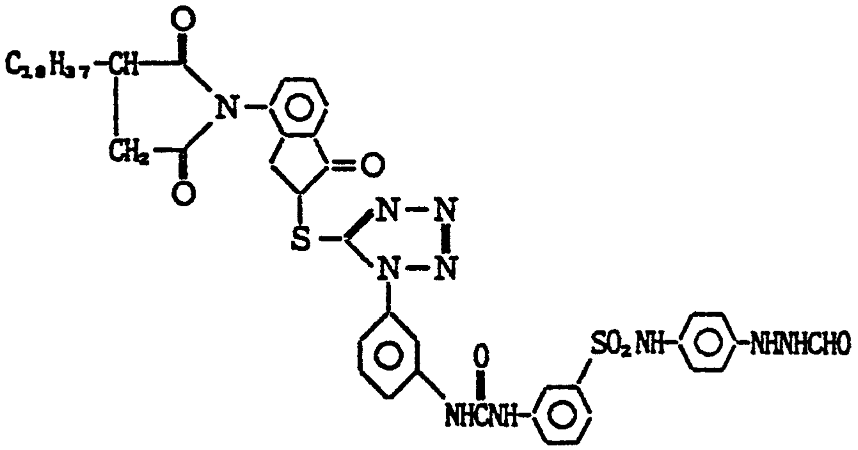
[4-13]


CH3
CH3-C-COCHCONH-
CH3
CO2C12H25(n)
Cl
S
N
N
N-
CH3
SO2NH-
-NHNHCHO
CONH-

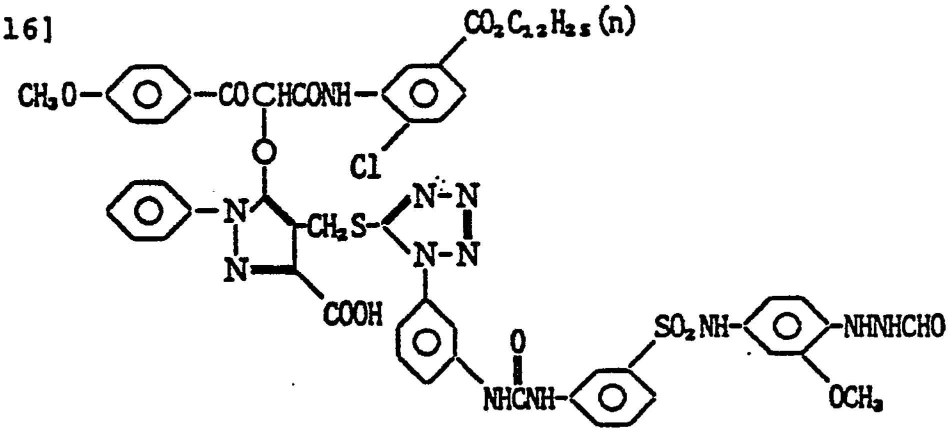
[4-14]


O
-S-
N-N
N-N
(t)C5H11-
-OCH2CNH
O
C5H11(t)
SO2NH-
-NHNHCHO

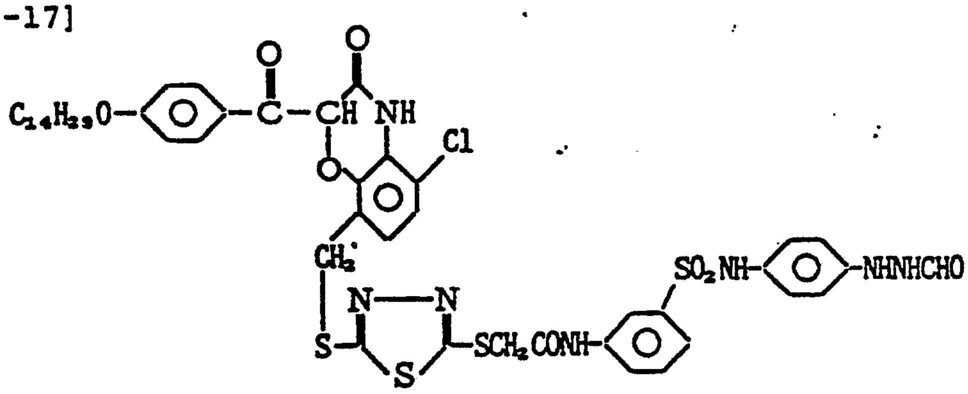
[4-15]


O
C18H37-CH
N-
CH2
O
=O
S
N-N
N-N
O
NHCNH-
SO2NH-
-NHNHCHO

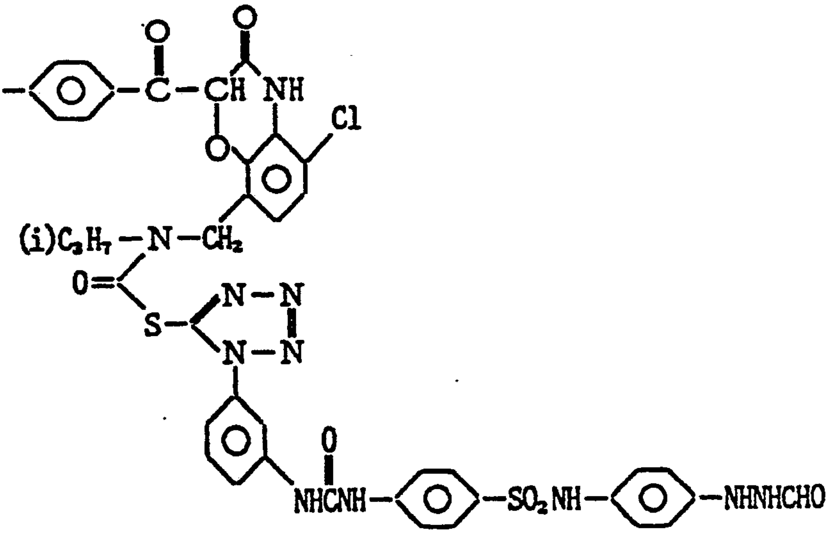
[4-16]



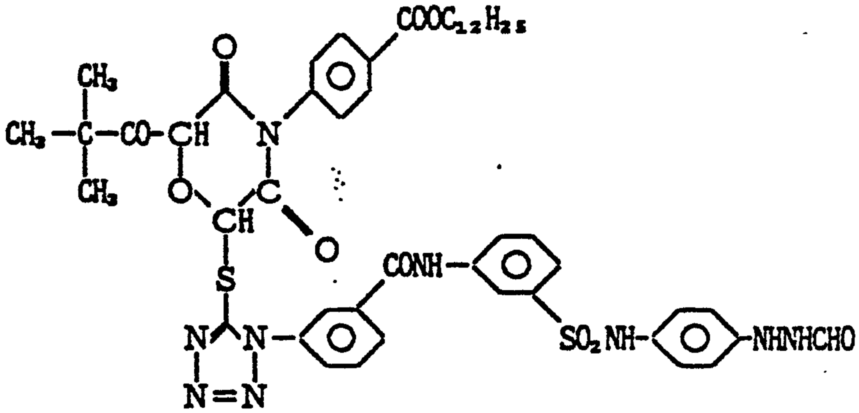
[4-17]



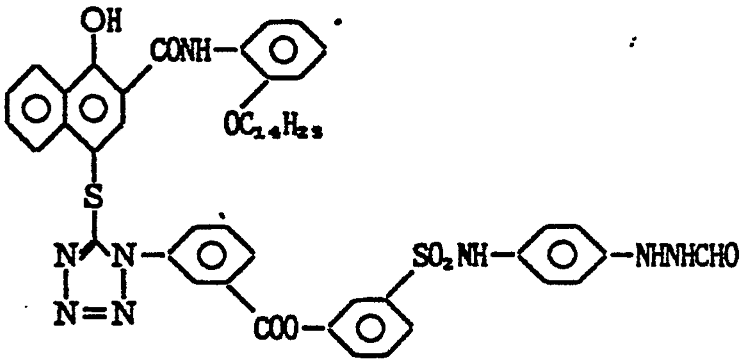
[4-18]



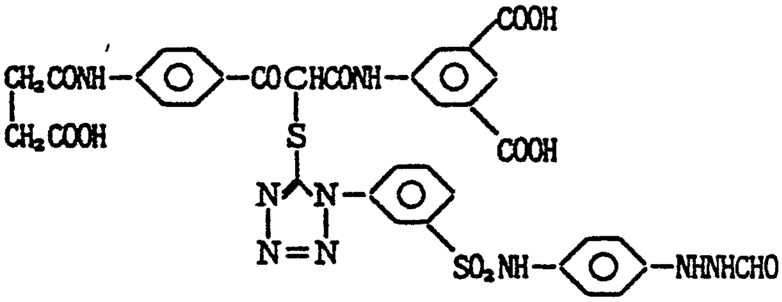
[4-19]


COOC₁₂H₂₅
CH₃
CH₃—C—CO—CH
CH₃
O
N
C
CH
O
S
CONH—
SO₂NH—
—NHNHCHO
N
N
N=N

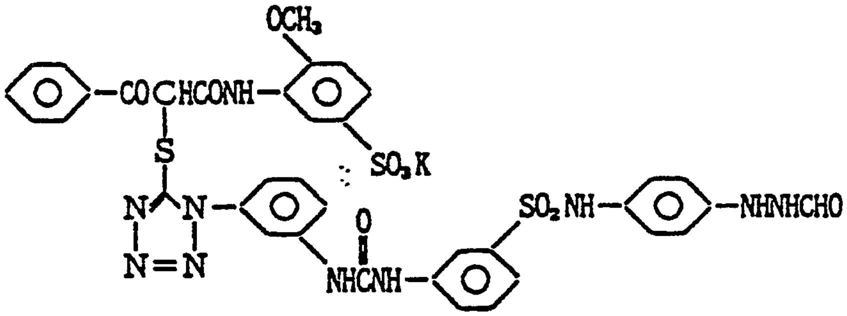
[4-20]


OH
CONH—
OC₁₄H₂₉
S
N
N—
N=N
SO₂NH—
—NHNHCHO
COO—

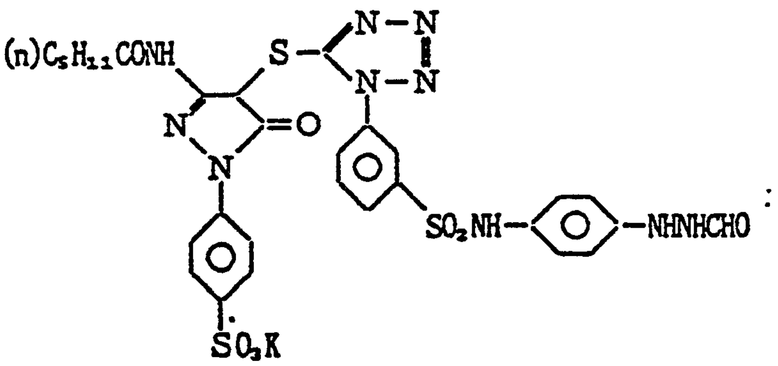
[4-21]


CH₂CONH—
CH₂COOH
—COCHCONH—
COOH
COOH
S
N
N—
N=N
SO₂NH—
—NHNHCHO

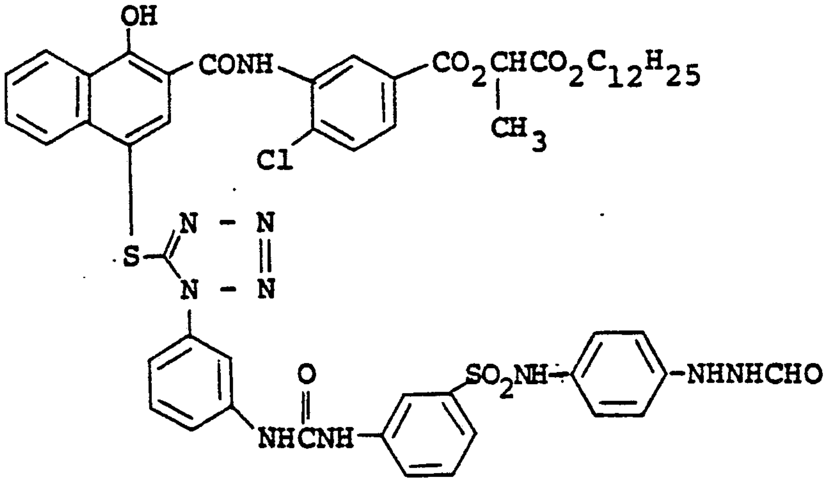
[4-22]


OCH₃
COCHCONH
S
SO₃K
N
N
N=N
O
NHCNH
SO₂NH
NHNHCHO

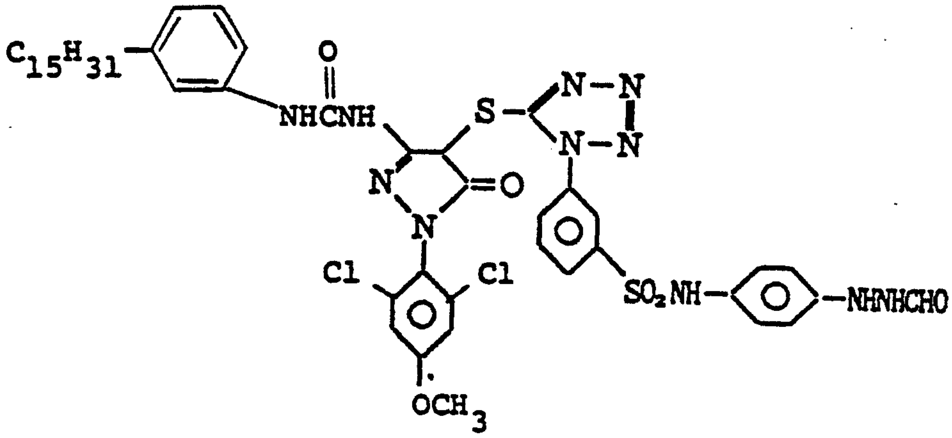
[4-23]


(n)C₅H₁₁CONH
S
N−N
N−N
N
N
=O
SO₂NH
NHNHCHO
SO₃K

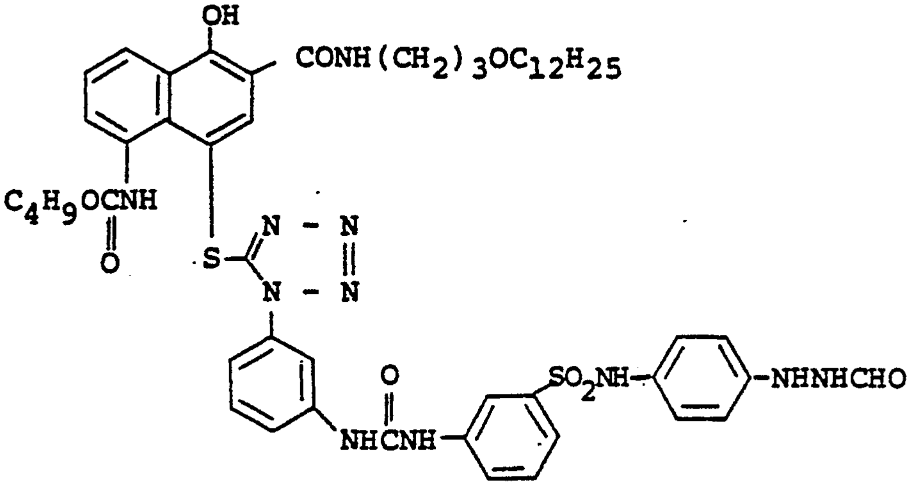
[4-24]


OH
CONH
CO₂CHCO₂C₁₂H₂₅
CH₃
Cl
S
N − N
N − N
O
NHCNH
SO₂NH
NHNHCHO

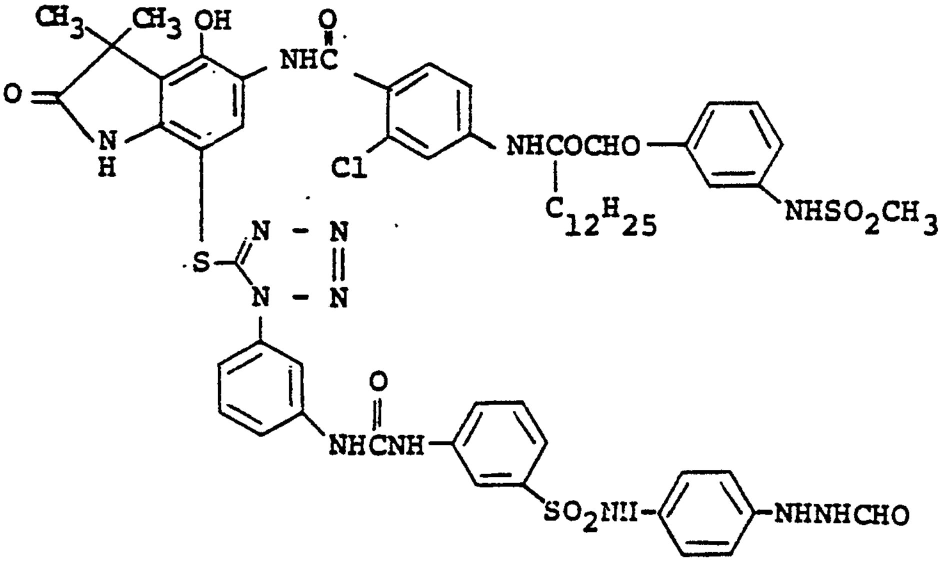
[4-25]


$C_{15}H_{31}$
O
NHCNH
S
N
N
N
N
N
N
O
Cl
Cl
OCH_3
SO_2NH
NHNHCHO

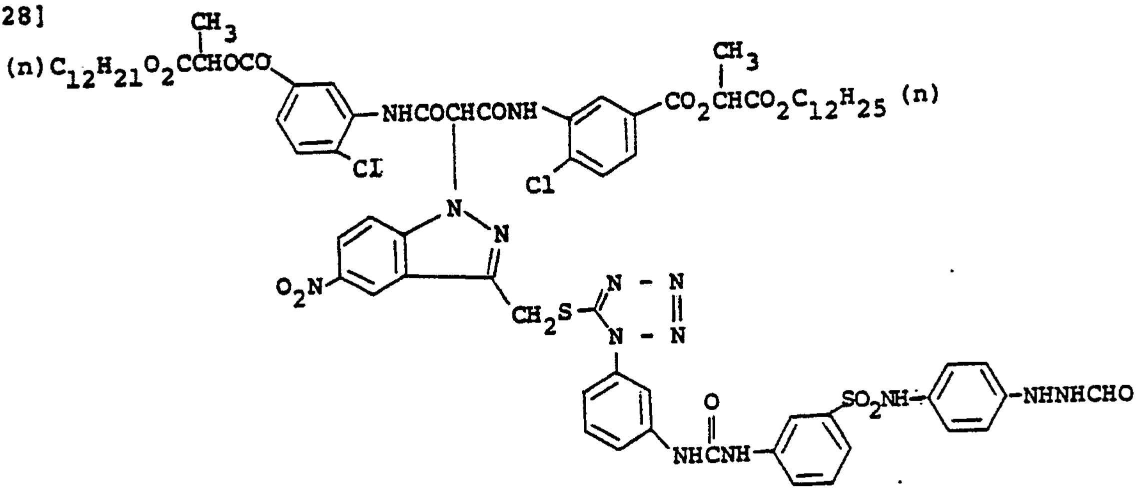
[4-26]


OH
$CONH(CH_2)_3OC_{12}H_{25}$
C_4H_9OCNH
O
S
N
N
N
N
O
NHCNH
SO_2NH
NHNHCHO

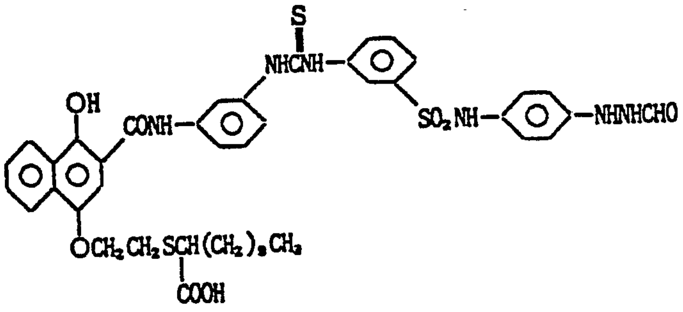
[4-27]


CH_3
CH_3
OH
O
NHC
O
N
H
Cl
NHCOCHO
$C_{12}H_{25}$
$NHSO_2CH_3$
S
N
N
N
N
O
NHCNH
SO_2NH
NHNHCHO

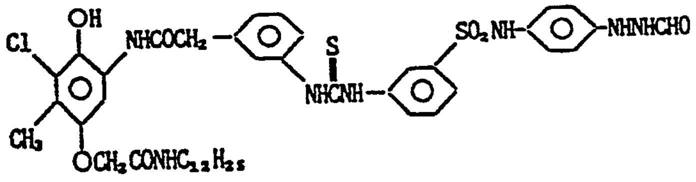
[4-28]



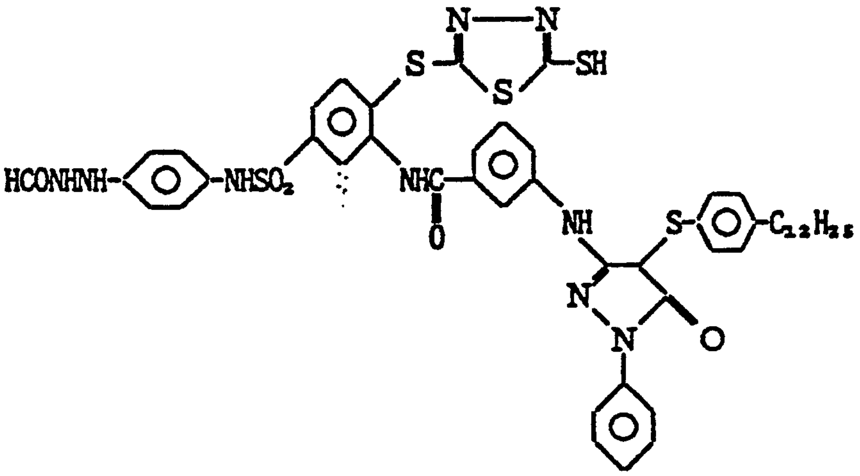
[5-1]



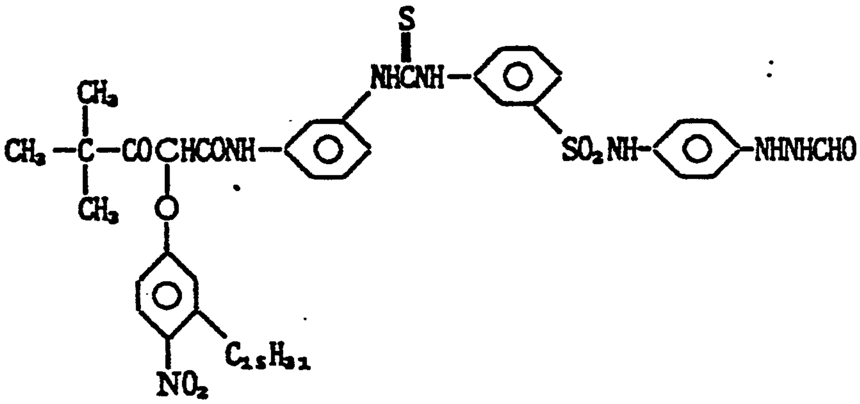
[5-2]



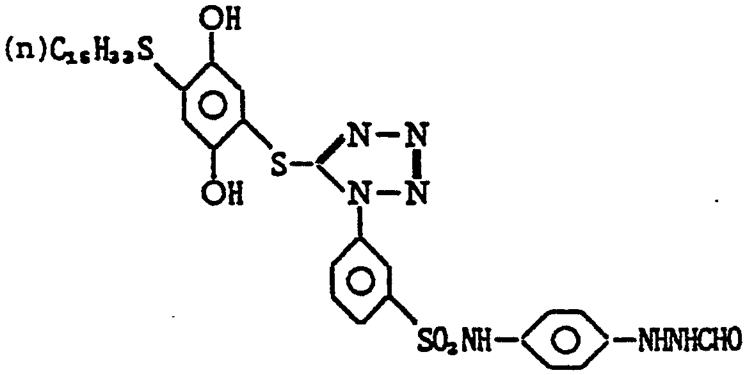
[5-3]



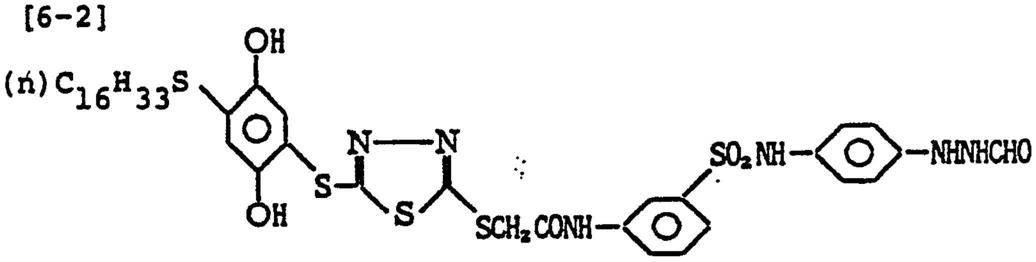
[5-4]



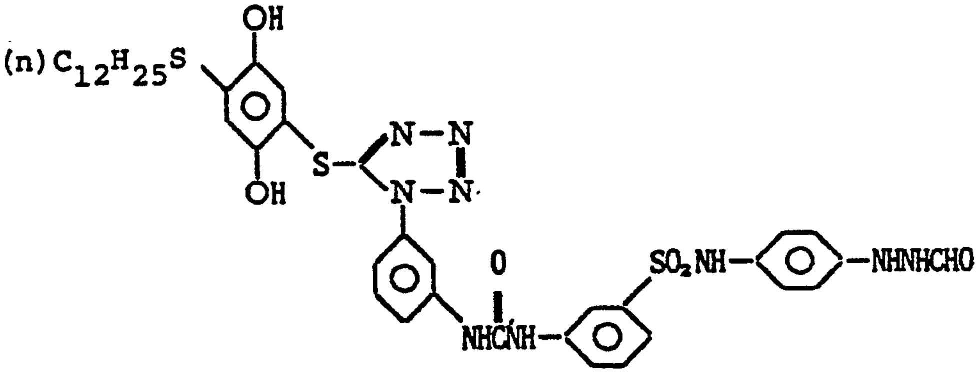
[6-1]



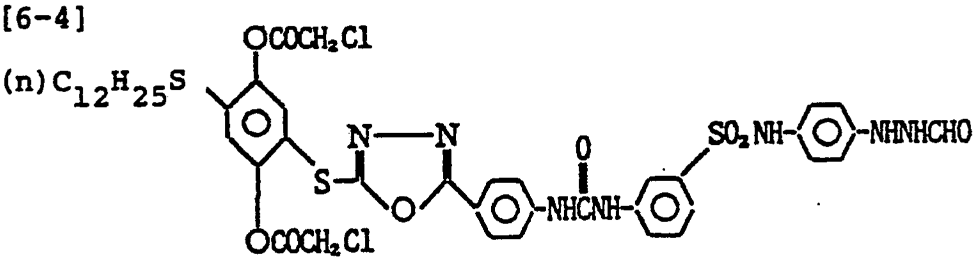
[6-2]


OH
(n)C16H33S
N
N
S
S
OH
SCH2CONH
SO2NH
NHNHCHO

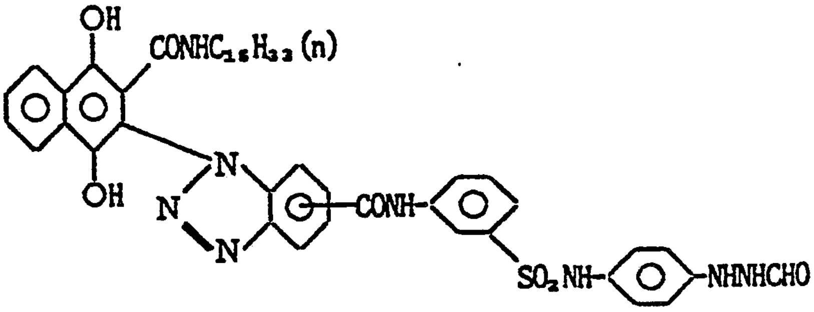
[6-3]


OH
(n)C12H25S
S
N
N
N
N
OH
O
NHCNH
SO2NH
NHNHCHO

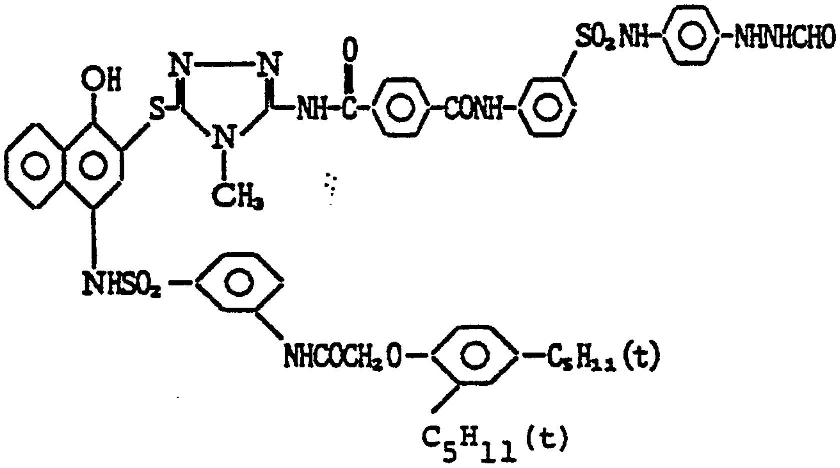
[6-4]


OCOCH2Cl
(n)C12H25S
N
N
S
O
O
NHCNH
SO2NH
NHNHCHO
OCOCH2Cl

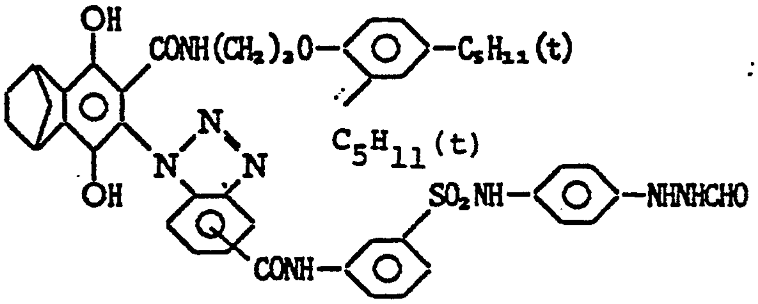
[6-5]


OH
CONHC16H33(n)
N
N
N
OH
CONH
SO2NH
NHNHCHO

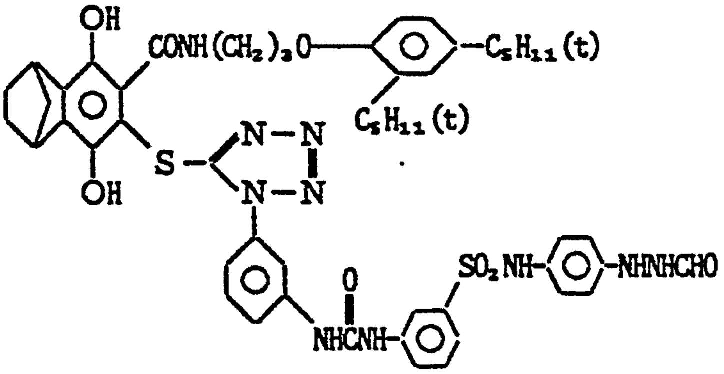
[6-6]


OH
S
N
N
N
CH3
O
NH-C
CONH
SO2NH
NHNHCHO
NHSO2
NHCOCH2O
C5H11(t)
C5H11(t)

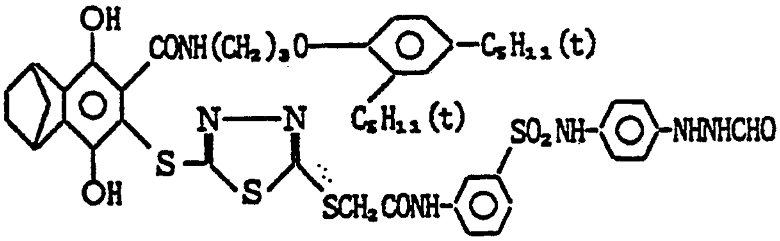
[6-7]


OH
CONH(CH2)3O
C5H11(t)
C5H11(t)
N
N
N
OH
SO2NH
NHNHCHO
CONH

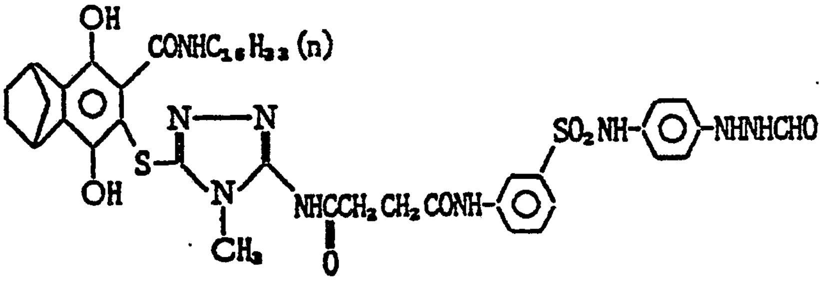
[6-8]


OH
CONH(CH2)3O
C5H11(t)
C5H11(t)
S
N-N
N-N
OH
O
NHCNH
SO2NH
NHNHCHO

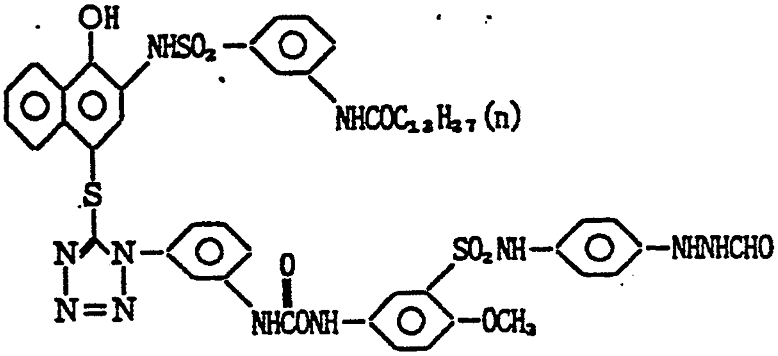
[6-9]



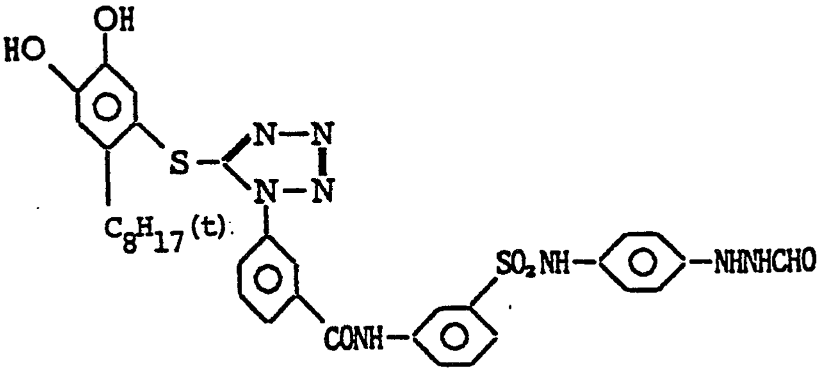
[6-10]



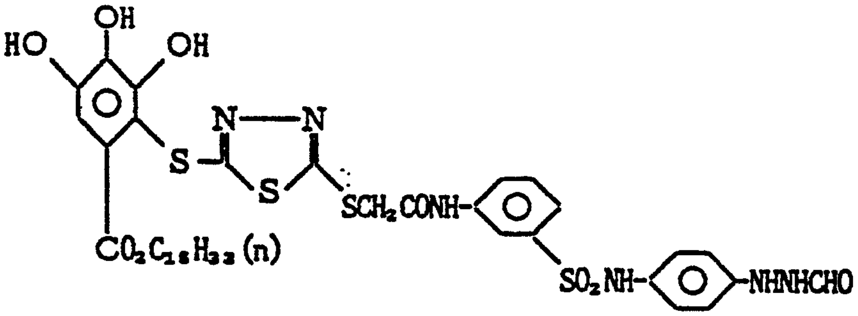
[6-11]



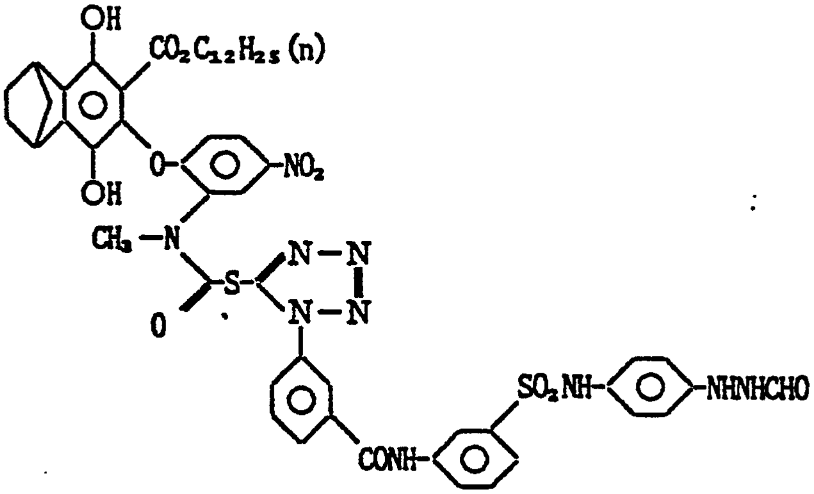
[6-12]



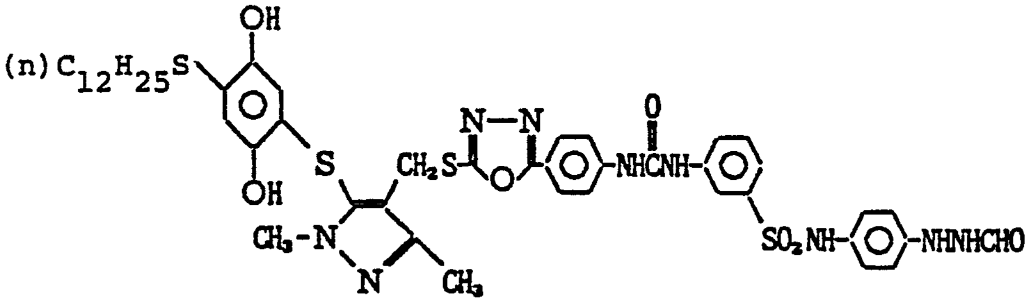
[6-13]



[6-14]



[6-15]



Preferable compounds of the above compounds are [1-1] to [1-18], [3-1] to [3-15], [4-1] to [4-23], and [6-1] to [6-15], and more preferable compounds are [4-1] to [4-23] and [6-1] to [6-15].

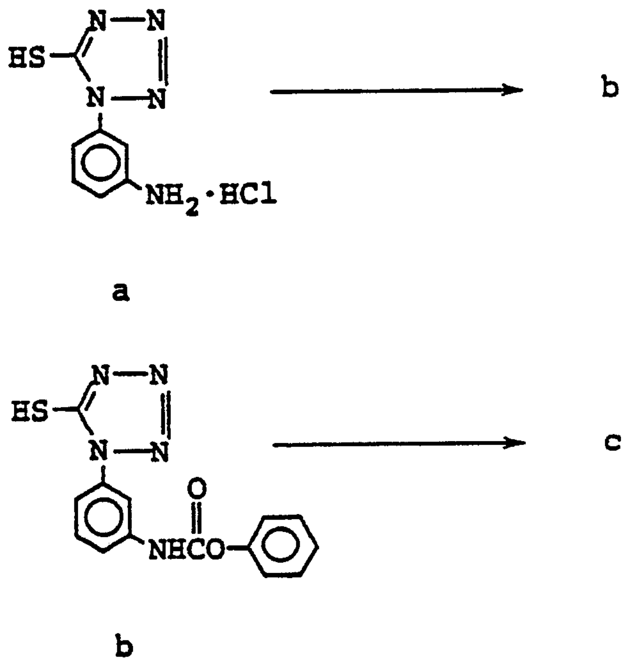
The compounds of the present invention can be prepared by methods which are similar to those disclosed in, for example, JP-A-57-150845, 59-157638 and 60-107029.

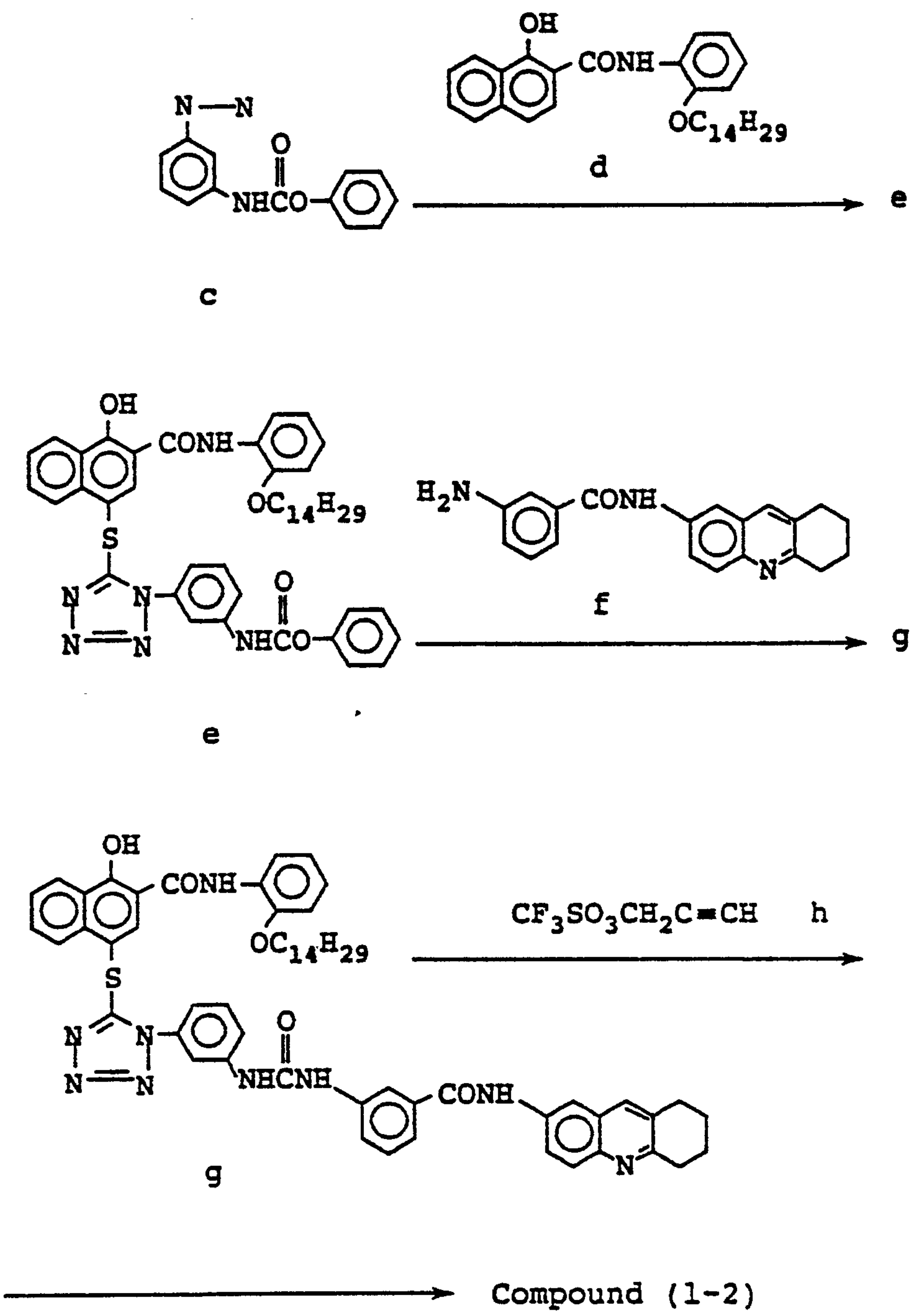
The FR compounds can be prepared by the methods disclosed in, for example, patent publications as referred to in Research Disclosure No. 22,534 (published on January, 1983), pages 50 to 54 and U.S. Patent 4,471,044, or by methods which are similar to these methods.

specific methods for the preparation of the compounds will be described below.

1. Production of Compound (1-2):

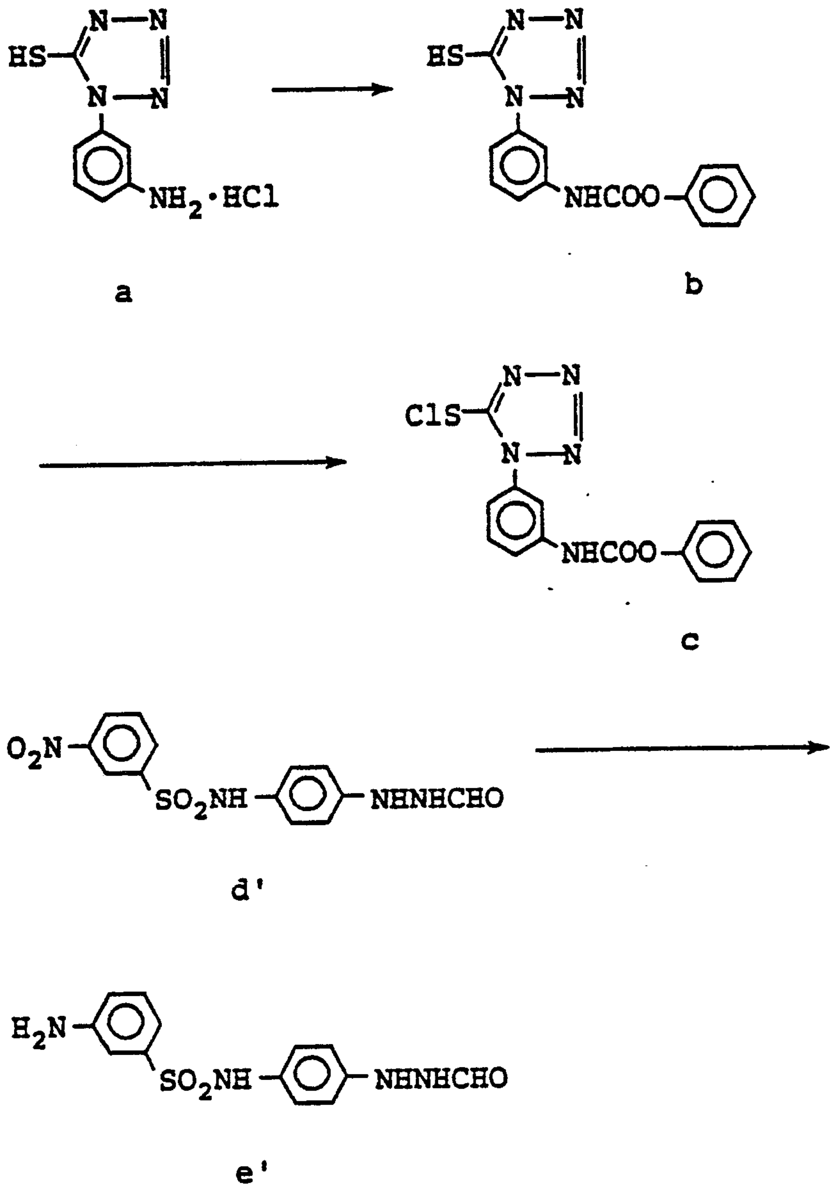
Production Route (1):

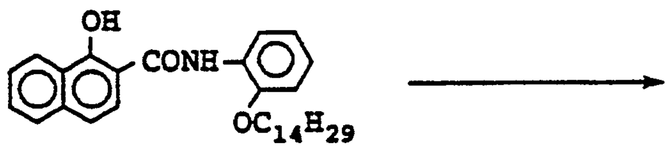




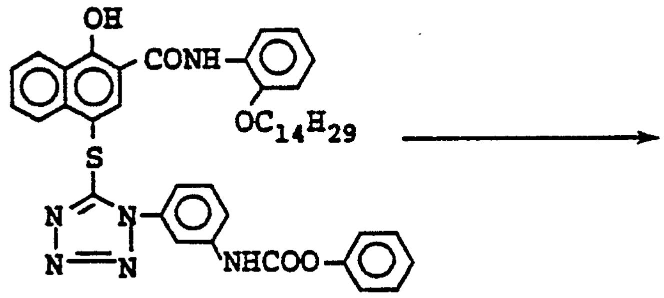
2. Production of Compound (4-1):

Production Route (2):

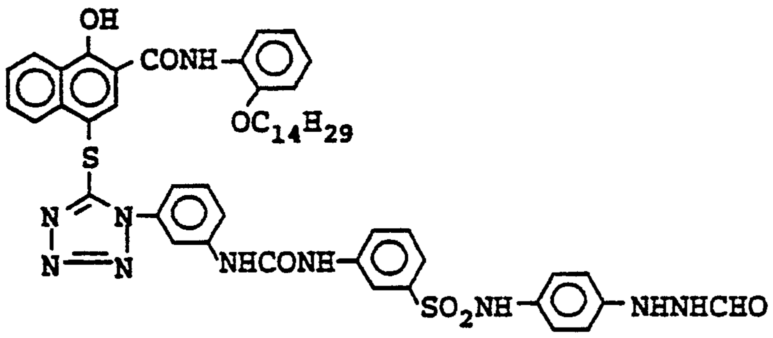




f'



g'



Compound (4-1)

1-1. Production of Compound (b):

A mixture comprising Compound (a) (22.9 g, 0.1 M), CH_3CN (150 ml) and pyridine (17.1 ml, 0.22 M) was stirred with cooling with ice, and phenyl chlorocarbonate (17 g, 0.105 M) was dropwise added thereto with keeping at 5° C or lower. After the addition, the whole was stirred fro 30 minutes at 5° C and then for 1 hour at room temperature. Then this was extracted with 500 ml of ethyl acetate, 10 ml of concentrated sulfuric acid and 300 ml of water. The resulting extract was washed twice with water and then dried with Glauber's salt and concentrated with an evaporator. 230 ml of acetonitrile was added and heated and then cooled, and the crystal precipitated was filtered to obtain 23.8 g of the Compound (b). Yield: 75%.

1-2. Production of Compound (c)

The Compound (b) (15.7 g, 0.05 M) was dispersed in methylene chloride (150 ml) and sulfuryl chloride (7.4 g, 0.55 M) was dropwise added thereto at 5° C or lower while cooling with ice. After the addition, the whole was stirred for 30 minutes at 5° C or lower and then for 1 hour at 15° C or lower. Then the methylene chloride was evaporated out by an aspirator under reduced pressure to obtain an oily product of the compound (e):

1-3. Production of Compound (e):

The Compound (d) (21.4 g, 0.045 M) was dissolved in chloroform (150 ml), and a 100 ml chloroform solution containing Compound (c) (17.4 g, 0.05 M) was dropwise added thereto over a period of about 15 minutes with cooling with ice to 5° C or lower. After the addition, the whole was stirred for 30 minutes at 5° C or lower and then for 1 hour at room temperature. Then the reaction solution was concentrated under reduced pressure. Ethyl acetate (300 ml) was added to the resulting residue to dissolve the same. After being washed with water, the solution was dried with Glauber's salt and concentrated. Acetonitrile was added to the residue for crystallization to obtain the Compound (e) (30.4 g). Yield: 86%.

1-4. Production of Compound (g):

Acetonitrile (50 ml) was added to the Compound (e) (7.9 g, 0.01 M), the Compound (f) (3.5 g, 0.011 M) prepared by the method described in Japanese Patent Application No. 62-17984 and imidazole (0.1 g), and heated under reflux for 4 hours in a nitrogen stream, whereupon the reaction solution changed from a non-homogeneous solution to a homogeneous solution. Ethyl acetate (150 ml) was added to the reaction solution, and it was washed three times with water and then dried with Glauber's salt and concentrated. Methanol was added to the residue for crystallization to obtain 7.6 g of the intended Compound (g). Yield: 75%.

1-5. Production of Compound (e′):

Iron powder (16.8 g) and ammonium chloride (1.7 g) were added to a mixed solution of isopropanol (120 ml) and water (17 ml) and heated under reflux in a nitrogen stream, and then the Compound (d′) was gradually added thereto in the form of a powder. After the addition, the whole was further heated for 1 hour under reflux, and then the reaction solution was filtered. The resulting filtrate was cooled with ice to obtain 13.3 g of the Compound (e′). Yield: 86.9%. m.p. 154 to 156° C.

1-6. Production of Compound (g′):

The compound (f′)(21.4 g, 0.045 M) was dissolved in chloroform (150 ml), and a 100 ml of chloroform solution containing 17.4 g (0.05 M) of the Compound (c) was dropwise added thereto over a period of about 15 minutes with cooling with ice to 5° C or lower. After the addition, the whole was stirred for 30 minutes at 5° C and then for 1 hour at room temperature. Then the reaction solution was concentrated under reduced pressure. Ethyl acetate (300 ml) was added to the resulting residue to dissolve the same, and the resulting solution was washed with water and then dried with Glauber's salt and concentrated. Acetonitrile was added to the residue for crystallization to obtain 30.4 g of the Compound (g′). Yield: 86%.

1-7. Production of Compound (1-2):

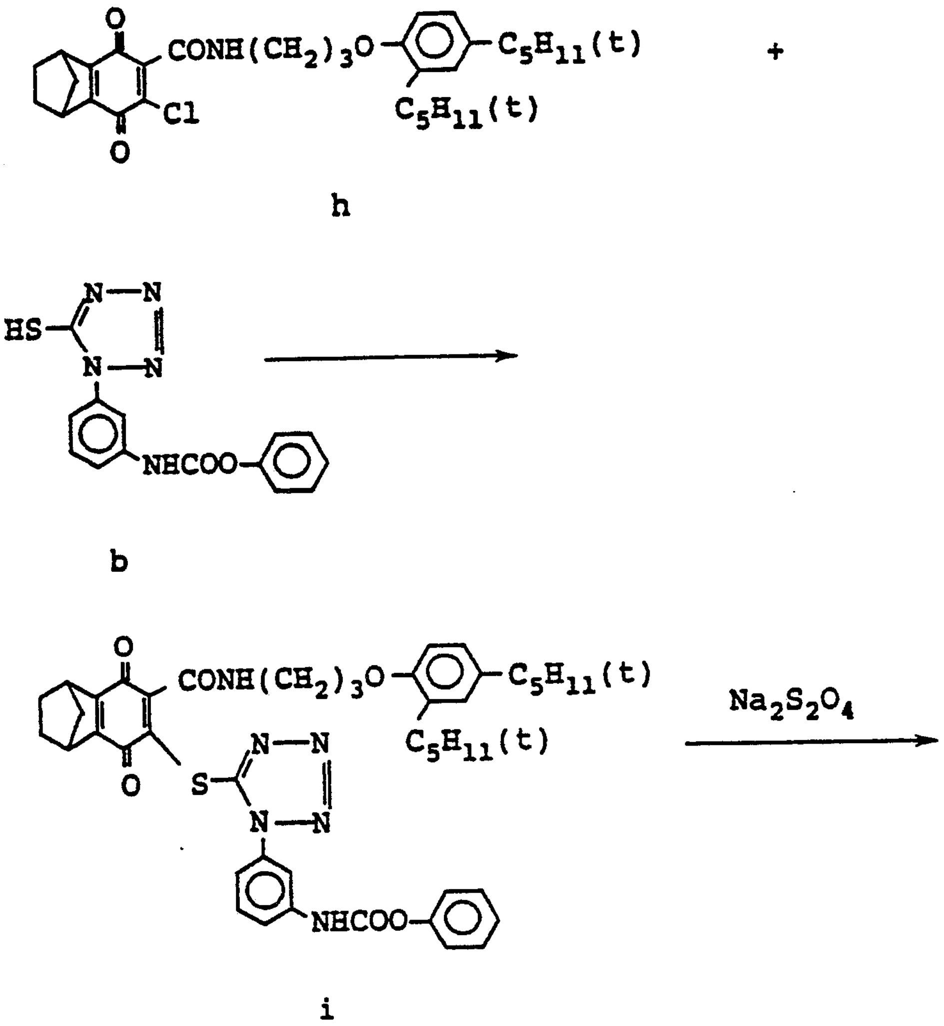
The compound (g) (5.6 9, 0.0056 M) was added to a carbon tetrachloride solution (40 ml) containing the Compound (h) (0.0070 M) as prepared by the method described in U.S. Patent 4,471,044, and the whole was heated under reflux for 2 hours. After spontaneously cooling, the reaction mixture was subjected to decantation to take out the tar product separated. This was washed twice with ether (10 ml), to obtain a crystal of the intended Compound (1-2). Yield: 4.2 g (63%) m.p. 100° C or more.

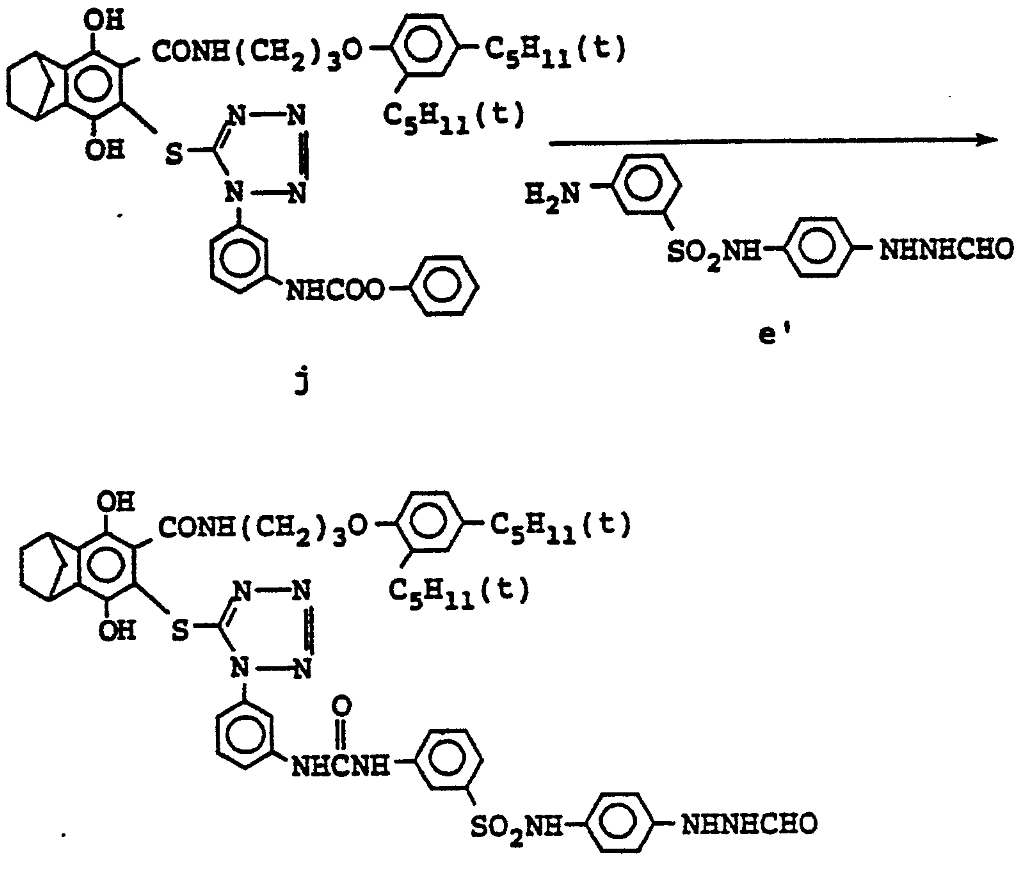
1-8. Production of Compound (4-1):

Acetonitrile (50 ml) was added to the Compound (g) (7.9 g, 0.01 M), the compound (e) (3.4 g, 0.011 M) and imidazole (0.1 g) and heated under reflux for 4 hours in a nitrogen stream, whereupon the reaction solution changed from a non-homogeneous solution to a homogeneous solution. Ethyl acetate (150 ml) was added to the reaction solution, which was then washed three times with water and dried with Glauber's salt and concentrated. Methanol was added to the residue for crystallization to obtain the intended Compound (4-1) (6 g). Yield: 60%. m.p. 176 to 178° C (decomposition).

2. Production of Compound (6-8):

Production Route:





Compound (6-8)

2-1. Production of Compound (j):

The compound (h) (26.3 g, 0.05 M) prepared by the method described in JP-A-61-230135 and Compound (b) (15.7 g, 0.05 M) were dissolved in acetone (300 ml) and reacted fro 3 hours at room temperature. The acetone was evaporated out from the reaction mixture under reduced pressure to obtain 34.5 g of a glassy product of Compound (i). Compound (i) was dissolved in ethyl acetate (150 ml) and a 150 ml aqueous solution of $Na_2S_2O_4$ (35 g) was added thereto and reacted fro 1 hour at room temperature with stirring. The ethyl acetate layer was separated, washed with water and concentrated under reduced pressure to obtain 33.1 g of a glassy product of the Compound (j). Yield: 92%.

2-2. Production of Compound (6-8):

By the same method as that for preparation of the Compound (4-1) mentioned in the previous step (1-8), the Compound (6-8) was also prepared. Yield: 45%.

Preferred embodiments of the present invention are as follows:

(1) Among the compounds represented by formulae (1) to (3), those represented by formulae (1) and (3) are preferred. The aforesaid colorless Compounds (1-14) and (1-15) for the formula (1) have somewhat less activity than the other coloring compounds.

(2) All the compounds of the formulae (1) to (3) can effectively be used for photographic materials to be developed with a color developer such as paraphenylenediamine or the like, for example, color autopositive or color negative photographic materials. Preferably, the compounds of formulae (1) and (3) are used, and more preferably, the compounds of formula (3) are used.

(3) The compounds of formula (3) are effectively used for photographic materials to be developed with a black-and-white developing agent such as 3-pyrazolidone-type or hydroquinone-type developing agent, for example, black-and-white autopositive photographic materials, autopositive micro-photographic materials, black-and-white negative photographic materials and high contrast negative photographic materials having a hydrazine-type nucleating agent.

(4) The compounds of the present invention are especially preferably applied to autopositive photographic materials.

The amount of the compound of the above-mentioned formulae (1) to (3) to be added to silver halide photographic materials in accordance with the present invention is from about 10^{-9} to about 10^{-1} mol, preferably from about 10^{-5} to about 10^{-1} mol, per mol of the silver of the silver halide contained in the layer containing the compound or in an adjacent layer.

For introduction of the compound into the silver halide emulsion layer of the photographic material of the present invention, any known method, for example, the method described in U.S. Patent 2,322,027 can be employed. For instance, the compound is first dissolved in a solvent, such as an alkyl phthalate (e.g., dibutyl phthalate, dioctyl phthalate), a phosphate (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, dioctylbutyl phosphate), a citrate (e.g., tributyl acetylcitrate), a benzoate (e.g., octyl benzoate), an alkylamide (e.g., diethyllaurylamide), a fatty acid ester (e.g., dibutoxyethyl succinate, diethyl azelate), a trimesate (e.g., tributyl trimesate) or the like, or in an organic solvent having a boiling point of from about 30°C to about 150°C, such as a lower alkyl acetate (e.g., ethyl acetate, butyl acetate), ethyl propionate, secondary butyl alcohol, methyl isobutyl ketone, β-ethoxyethyl acetate, methyl cellosolve acetate or the like, and then the resulting solution is dispersed in a hydrophilic colloid. The above-mentioned high boiling point organic solvent and low boiling point organic solvent may be used in the form of a mixture thereof.

In addition, the dispersion method with a polymer, which is described in JP-B-51-39853 and JP-A-51-59943, may also be employed.

When the above-mentioned compound has an acid group such as carboxylic acid group or a sulfonic acid group, this may be introduced into a hydrophilic colloid in the form of an alkaline aqueous solution of the compound.

In the photographic emulsions of the photographic materials of the present invention, any silver halide including silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide and silver chloride may be used.

The silver halide grains in the photographic emulsion may be regular grains having a regular crystalline form such as a cubic, octahedral or tetradecahedral crystalline form, or irregular grains having an irregular crystalline form such as a spherical crystalline form or having a crystal defect such as a twin plane, or may also be grains having a composite form of these crystalline forms. In addition, a mixture of grains with various crystalline forms may be used.

Regarding the grain size of the silver halide grains, the grains may be fine grains having a grain size of about 0.1 µm or less or may be large grains having a grain size, as a diameter of the projected area, of up to about 10 µm. The emulsion may be either a monodisperse emulsion having a narrow grain size distribution of a polydisperse emulsion having a broad grain size distribution.

The silver halide photographic emulsions for use in the present invention can be prepared by any conventional method, for example, in accordance with the methods described in Research Disclosure, Vol. 176, No. 17643 (December, 1978), pages 22 to 23, "1. Emulsion Preparation and Type" and ibid., Vol. 187, No. 18716 (November, 1979), page 648.

The photographic emulsions for use in the present invention can also be prepared in accordance with the methods described in P. Glafkides, Chemie et Physique Photographique (published by Paul Montel, 1967); G.F. Duffin, Photographic Emulsion Chemistry (published by Focal Press, 1966); V.L. Zelikman et al., Making and Coating Photographic Emulsion (published by Focal Press, 1954), etc. For example, the silver halide emulsions may be prepared by an acid method, a neutralization method, or an ammonia method. Also, as a method of reacting a soluble silver salt and soluble halide(s), a single jet method, a double jet method, or a combination thereof may be used. A reverse mixing method capable of forming silver halide grains in the presence of excess silver ions can also be employed. As one double jet method, a controlled double jet method of keeping a constant pAg in a liquid phase for forming silver halide grains can also be employed. According to the method, a silver halide emulsion containing silver halide grains having a regular crystal form and almost uniform grain sizes can be obtained.

The silver halide emulsions for use in the present invention can be physically ripened in the presence of a known silver halide solvent (for example, ammonia or potassium thiocyanate, as well as the thioethers and thione compounds described in U.S. Patent 3,271,157, and JP-A-51-12360, JP-A-53-82408, JP-A-53-144319, JP-A-54-100717 and JP-A-54-155828. According to this method, a silver halide emulsion containing silver halide grains having a regular crystal form and almost uniform grain sizes can also be obtained.

The above-mentioned silver halide emulsion containing regular crystal grains may be obtained by properly controlling the pAg value and the pH value in the formation of the grains. The details are described in, for example, Photographic Science and Engineering, Vol. 6, poages 159 to 165 (1962); Journal of Photographic Science, Vol. 12, pages 242 to 251 (1964); and U.S. Patent 3,655,394 and British Patent 1,413,748.

As the monodisperse emulsion for use in the present invention, an emulsion in which the silver halide grains have a mean grain size (diameter) larger than about 0.05 µm and at least 95% by weight of the grains have a grain size falling within the range of the mean grain size ±40% is typical. Further, an emulsion in which the silver halide grains have a mean grainsize of from 0.15 to 2 µm and at least 95% by weight or by number of the grains have a grain size falling within the range of the mean grain size ±20% can also be used. The method of preparing such emulsions is described in U.S. Patents 3,574,628 and 3,655,394 and British Patent 1,413,748. In addition, the monodisperse emulsions described in JP-A-48-8600, JP-A-51-39027, JP-A-51-83097, JP-A-53-137133, JP-A-54-48521, JP-A-54-99419, JP-A-58-37635, JP-A-58-49938 are also preferably used.

Also, tabular grains having an aspect ratio of 5 or more may be used in the present invention. Tabular grains can easily be prepared by the methods described in Gutoff, Photographic Science and Engineering, Vol. 14, pages 248 to 257 (1970); and U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520 and British Patent 2,112,157. Tabular grains are preferably used since the coating power of the emulsion is elevated and the color-sensitizing efficiency by sensitizing dyes is elevated, and the details are mentioned in the aforesaid U.S. Patent 4,434,226.

In the formation of the silver halide grains for use in the present invention, a sensitizing dye or an additive can be added to the grains so as to properly control the crystal form of the grains formed.

The crystal structure of the grains may be uniform, or the inner part and the outer part of the grain may have different halogen compositions. The grain may also have a layered structure. These emulsion grains are illustrated in British Patent 1,027,146, U.S. Patents 3,505,068 and 4,444,877 and Japanese Patent Application No. 58-248469. Silver halides of different compositions may be combined by epitaxial junction, or the grains may also be combined with any other compounds than silver halides, such as silver thiocyanate or lead oxide, by a junction structure. The emulsion grains of this type are illustrated in U.S. Patents 4,094,684, 4,142,900 and 4,459,353, British Patent 2,038,792, U.S. Patents 4,349,622, 4,395,478, 4,433,501, 4,463,087, 3,656,962 and 3,852,067 and JP-A-59-162540.

Further, internal latent image-type grains formed by surface chemical ripening of silver halide grains to give a light-sensitive nucleus (e.g., Ag_2S, AgN, Au) in the grain crystal and then growing a silver halide layer around the nucleus can also be used in the present invention.

The silver halide grains may also be formed or physically ripened in the presence of a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof, anion salt or a complex salt thereof.

The various kinds of emulsions may be surface latent image-type emulsions which form a latent image mainly on the surface of the grain or internal latent image-type emulsions which form a latent image mainly in the inside of the grain.

The emulsion may also be a direct reversal emulsion. The direct reversal emulsion may be any of a solarization-type, an internal latent image-type, an optical fog-type or a nucleating agent containing-type, or a combination thereof.

The emulsions are illustrated, for example, in H. James The theory of the Photographic Process fourth edition, page 170, US Patents 2,592,250, and 2,466,957, British Patent 1,151,363 and Research Disclosure Vol.151, No. 15162 (15 November, 1976) pages 76 to 78.

Among them, it is preferred that a non-previously fogged internal latent image type emulsion is used, and this is fogged with a light before or during photographic processing or a nucleating agent is used to obtain a direct positive color photographic material.

The non-previously fogged internal latent image-type silver halide emulsion for use in the present invention is such that the surface of the silver halide grain is not previously fogged and a latent image is formed mainly in the inside of the grain. More specifically, the term "internal latent image" emulsion as used herein is emulsion defined as follows. A silver halide emulsion in a certain amount is coated on a transparent support and this is exposed to a light for a fixed period of time of from 0.01 to 10 seconds. Then this is developed with the following Developer (A) (internal developer) for 6 minutes at 20°C and the maximum density obtained is measured by a conventional photographic densitometric method. On the other hand, the same silver halide is also coated in the same amount and then exposed in the same manner. This is then developed with the following Developer (B) (surface developer) for 5 minutes at 18°C and the maximum density obtained is also measured in the same manner. Preferably, the former maximum density is at least five times larger than the latter maximum density, and more preferably, the former is at least ten times larger than the latter.

Surface Developer B:

Metol	2.5 g
L-ascorbic Acid	10 g
$NaBO_2 \cdot 4H_2O$	35 g
KBr	1 g
Water to make	1 liter

Internal Developer A:

Metol	2 g
Sodium Sulfite (Anhydride)	90 g
Hydroquinone	8 g
Sodium Carbonate (Monohydrate)	52.5 g
KBr	5 g
KI	0.5 g
Water to make	1 liter

As examples of the internal latent image-type emulsion, there may be mentioned, for example, the conversion-type silver halide emulsions described in British Patent 1,011,062 and U.S. Patents 2,592,250 and 2,456,943, as well as core/shell type silver halide emulsions. Examples of core/shell type silver halide emulsions are described in JP-A-47-32813, JP-A-47 32814, JP-A-52-134721, JP-A-52-156614, JP-A-53-60222, JP-A-53-66218, JP-A-53-66727, JP-A 55-127549, JP-A-57-136641, JP-A-58-70221. JP-A-59-208540, JP-A-59-216136, JP-A-60-107641, JP-A-60-247237, JP-A-61-2148, JP-A-61 3137, JP-A-56-18939, JP-A-58-1412, JP A-58-1415, JP-A-58-6935 and JP-A-58-108528 and JP-B-61-36426, U.S. Patents 3,206,313, 3,317,322, 3,761,266, 3,761,276, 3,850,637, 3,923,513, 4,035,185, 4,395,478 and 4,504,570, European Patent 17,148, and Research Disclosure No. 16345 (November, 1977).

In order to remove soluble silver salts from the emulsion before and after physical ripening, the emulsion may be subjected to noodle washing, flocculation, precipitation or ultrafiltration.

The emulsions for use in the present invention are, in general, physical ripened, chemically ripened or spectrally ripened. The additives usable in the ripening steps are described in the above Research Disclosure No. 17643 (December, 1978) and No. 18716 (November, 1979), and the relevant parts are listed in the following Table.

Known photographic additives which can be used in the present invention are also described in these publications and the relevant parts are also listed in the following Table.

Kinds of Additives	RD 17643	RD 18716
1 Chemical Sensitizers	p. 23	p. 648 right column
2 Sensitivity-enhancer		"
3 Spectral Sensitizer Super Color Sensitizers	pp. 23-24	From p. 648 right column to p. 649 right column
4 Brightening Agent	p. 24	
5 Anti-foggant Stabilizer	pp. 24-25	p. 649 right column
6 Light Absorbant Filter Dye UV Absorbers	pp. 25-26	From p. 649 right column to p. 650, left column
7 Stain Inhibitor	p. 25, right column	p. 650, From left to right column
8 Color Image Stabilizer	p. 25	
9 Hardening Agent	p. 26	p. 651, left column
10 Binder	p. 26	"
11 Plasticizer Lubricant	p. 27	p. 650, right column
12 Coating Aid Surfactant	pp. 26-27	"
13 Antistatic Agent	p. 27	"

Various color couplers can be used in the present invention in addition to the coupler having Cp moiety of the present invention. Color couplers are compounds which can react with the oxidation product of an aromatic primary amine color developing agent by a coupling reaction to form or release a substantially non-diffusible dye, and these themselves are preferably substantially non-diffusible compounds. Specific examples of useful color couplers include naphthol or phenol compounds, pyrazolone or pyrazoloazole compounds and open-chain or heterocyclic ketomethylene compounds. Examples of these cyan, magenta and yellow couplers for use in the present invention are described in Research Disclosure No. 17643 (December, 1978), page 25, VII-D, ibid., No. 18717 (November, 1979) and Japanese Patent Application No. 61-32462, as well as in the publications referred to therein. The color couplers are preferably used in a larger amount than the coupler having Cp moiety of the present invention.

Above all, the yellow couplers for use in the present invention include oxygen atom releasing-type or nitrogen atom releasing-type 2-equivalent yellow couplers as typical examples. In particular, α-pivaloylacetanilide couplers are excellent in fastness, especially light fastness of colored dyes formed, while α-benzoylacetanilide couplers are excellent in coloring density.

The 5-pyrazolone magenta couplers which may be preferably used in the present invention include 5-pyrazolone couplers in which the 3 position is substituted by an arylamino group or an acylamino group (especially sulfur atom releasing-type 2-equivalent couplers).

Further preferred are pyrazoloazole couplers, and the pyrazolo[5,1-c][1,2,4]triazoles described in U.S. Patent 3,725,067 are especially preferred among them. In addition, the imidazo[1,2-b]pyrazoles described in U.S. Patent 4,500,630 are more preferred from the view point of the small yellow side-absorption and the high light-fastness of the colored dyes formed, and the pyrazolo[1,5 b][1,2,4]triazoles described in U.S. Patent 4,540,654 are particularly preferred.

The cyan couplers which can preferably be used in the present invention include the naphthol and phenol couplers described in U.S. Patents 2,474,293 and 4,052,212, and the phenol cyan couplers having an alkyl group of two or more carbon atoms at the meta-position of the phenol nucleus described in U.S. Patent 3,772,002. In addition, 2,5-diacylamino-substituted phenol couplers are also preferred from the viewpoint of the fastness of the color images formed.

Colored couplers for correcting any unnecessary absorption of the dyes formed in a short wavelength range, couplers, of forming dyes with a pertinent diffusibility, colorless couplers, DIR couplers of releasing a development inhibitor with coupling reaction and polymerized couplers can also be used in the present invention.

The standard amount of the color coupler for use in the present invention is from 0.001 to 1 mol per mol of the light-sensitive silver halide. Preferably, the amount is from 0.01 to 0.5 mol for an yellow coupler;

it is from 0.03 mol to 0.3 mol for a magenta coupler; and it is from 0.002 mol to 0.3 mol for a cyan coupler.

A coupler enhancer can be used in the present invention so as to improve the coloring capacity of the couplers used. Specific examples of the compounds as the enhancer are described in Japanese Patent Application No. 61-32462, pages 374 to 391.

For incorporation of the couplers into emulsion layers in accordance with the present invention, the coupler is first dissolved in a high boiling point organic solvent and/or a low boiling point organic solvent and then emulsified and dispersed in gelatin or in other aqueous hydrophilic colloid solution by high speed stirring with a homogenizer or the like, or by mechanical milling with a colloid mill or the like, or by means of an ultrasonical technique, and the resulting dispersion is added to the intended emulsion layer. In this case, the high boiling point organic solvent is not always necessary but the compounds described in Japanese Patent Application No. 61-32462, pages 440 to 467 are preferably used.

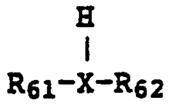
The couplers of the present invention can be dispersed in a hydrophilic colloid by the method described in Japanese Patent Application No. 61-32462, pages 468 to 475.

The photographic materials of the present invention preferably contain one or more compounds capable of reacting with formaldehyde gas to fix the same, which are described in detail hereunder.

The compounds capable of reacting with formaldehyde gas to fix the same (hereinafter referred to as "formalin scavenger") for use in the present invention are those represented by the following general formulae (SI) and (SII), which have a relative molecular weight of 300 or less per one unit of the active hydrogen in the molecule. The relative molecular weight is defined as follows:

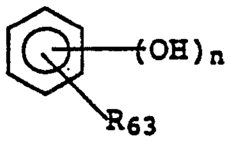
$$(\text{Relative Molecular Weight}) = \frac{(\text{Molecular Weight})}{(\text{Active Hydrogen in Molecule})}$$

(SI)



$$R_{61}-\overset{\overset{\displaystyle H}{|}}{X}-R_{62}$$

(SII)



In these formulae, R_{61} and R_{62} which may be the same or different, each represents hydrogen, an alkyl group, a substituted alkyl group; an aryl group, a substituted aryl group, an acyl group, an alkoxycarbonyl group, a carbamoyl group or an amino group, and R_{61} and R_{62} may be linked to form a ring, provided that at least one of R_{61} and R_{62} is an acyl group, an alkoxycarbonyl group, a carbamoyl group or an amino group;

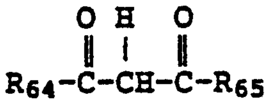
X represents $-\overset{|}{C}H-$ or $-\overset{|}{N}-$;

R_{63} represents hydrogen, an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group, and R_{63} may be linked to the phenyl ring to form a bicyclic compound;

n is an integer of 2 to 5.

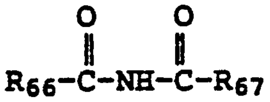
As the formalin scavenger of the formulae (SI) and (SII), preferred compounds are those represented by the following formulae (SI-1) to (SI-7) and (SII-1) and (SII-2), which include enol tautomers thereof, if any. Among the compounds of the formulae (SI) and (SII), those of the formula (I) are more preferred.

[SI-1]



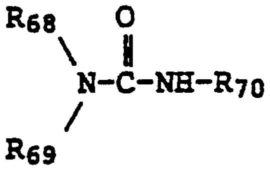
$$R_{64}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-R_{65}$$

[SI-2]



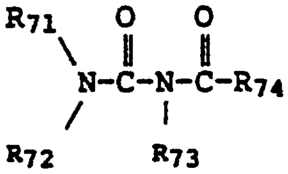
$$R_{66}-\overset{O}{\overset{\|}{C}}-NH-\overset{O}{\overset{\|}{C}}-R_{67}$$

[SI-3]



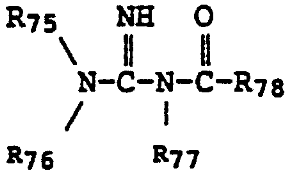
$$\begin{matrix}R_{68} & \\ & \diagdown \\ & N-\overset{O}{\overset{\|}{C}}-NH-R_{70} \\ & \diagup \\ R_{69} & \end{matrix}$$

[SI-4]



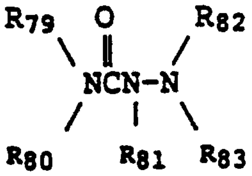
$$\begin{matrix}R_{71} & \\ & \diagdown \\ & N-\overset{O}{\overset{\|}{C}}-\underset{R_{73}}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-R_{74} \\ & \diagup \\ R_{72} & \end{matrix}$$

[SI-5]



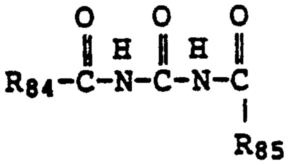
$$\begin{matrix}R_{75} & \\ & \diagdown \\ & N-\overset{NH}{\overset{\|}{C}}-\underset{R_{77}}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-R_{78} \\ & \diagup \\ R_{76} & \end{matrix}$$

[SI-6]



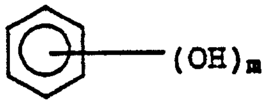
$$\begin{matrix}R_{79} & & & & R_{82} \\ & \diagdown & & \diagup & \\ & & N\overset{O}{\overset{\|}{C}}\underset{R_{81}}{\underset{|}{N}}-N & & \\ & \diagup & & \diagdown & \\ R_{80} & & & & R_{83}\end{matrix}$$

[SI-7]

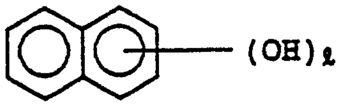


$$R_{84}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\overset{O}{\overset{\|}{\underset{R_{85}}{\underset{|}{C}}}}$$

[SII-1]



[SII-2]

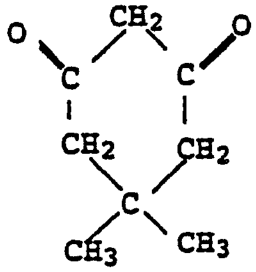


In these formulae, R_{64} to R_{85} which may be the same or different, each represents hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group, provided that at least one of R_{71}, R_{72}, R_{73} and R_{74} and at least one of R_{79} to R_{83}, represents a hydrogen atom.

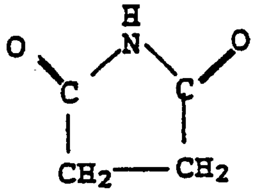
R_{64} and R_{65}; R_{66} and R_{67}; and R_{84} and R_{85} each may be linked to form a ring. Any two of each of R_{68} to R_{70}; R_{71} to R_{74}; R_{75} to R_{78}; and R_{79} to R_{83} may also form a ring. m is an integer of from 3 to 6; and ℓ is an integer of 2 or more.

Among the formalin scavengers of the formulae (SI-1) to (SI-7) and (SII-1) and (SII-2), especially preferred compounds include the following, but the present invention is not to be construde as being limited thereto.

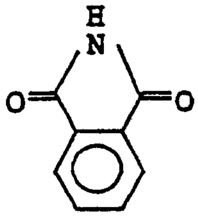
(S-1)



(S-2)

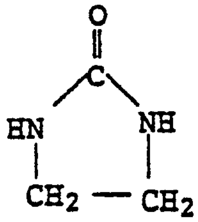


(S-3)

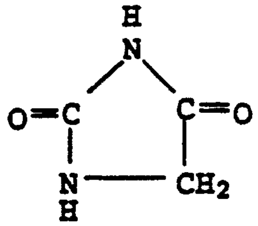


(S-4) $NH_2CONHCH_2CH_2NHCONH_2$

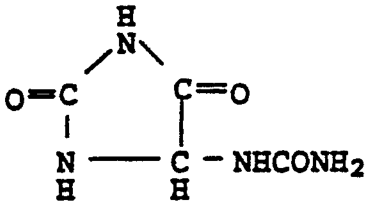
(S-5)



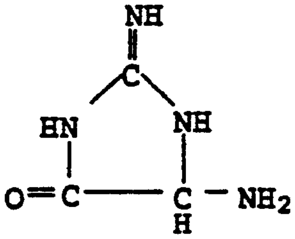
(S-6)



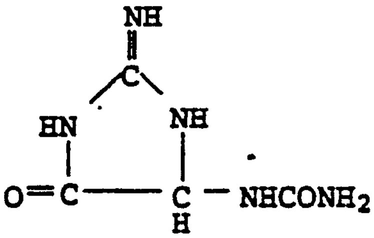
(S-7)



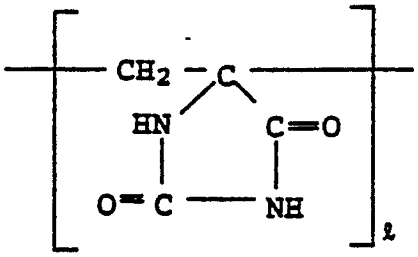
(S-8)



(S-9)



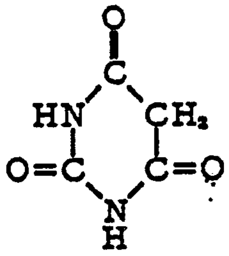
(S-10)



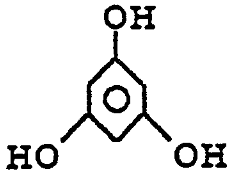
(S-11)

$H_2NC(=O)NHNH_2$

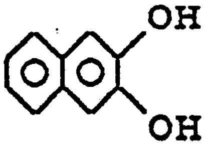
(S-12)



(S-13)



(S-14)



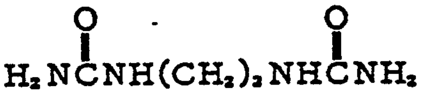
(S-15)

$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$

(S-16)

$H_2N\overset{O}{\overset{\|}{C}}NHCH_2NH\overset{O}{\overset{\|}{C}}NH_2$

(S-17)

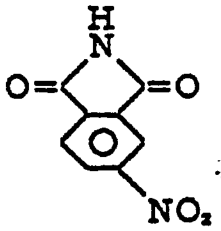


$H_2N\overset{O}{\overset{\|}{C}}NH(CH_2)_2NH\overset{O}{\overset{\|}{C}}NH_2$

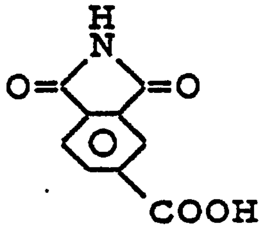
(S-18)

$C_2H_5NH\overset{O}{\overset{\|}{C}}NH_2$

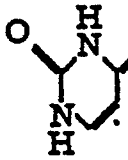
(S-19)



(S-20)



(S-21)



(S-22)

$CH_3\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}NH_2$

(S-23)

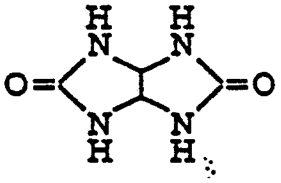
$CH_3\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}-NHCH_3$

(S-24)

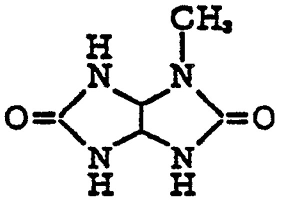
$C_2H_5NH\overset{O}{\overset{\|}{C}}NHNH_2$

(S-25) $CH_3CONHCONHCOCH_3$

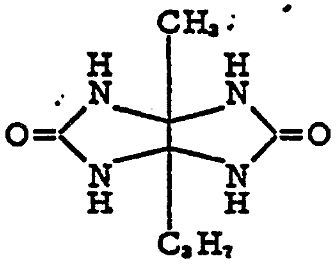
(S-26)



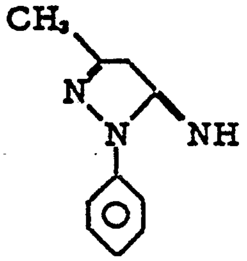
(S-27)



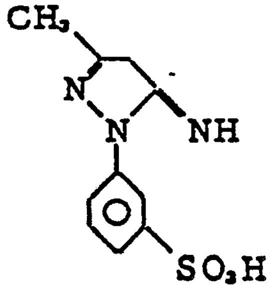
(S-28)



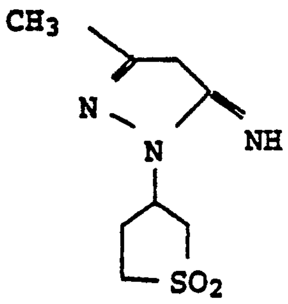
(S-29)



(S-30)



(S-31)



The above-mentioned Compound (S-10) is an oligomer or polymer having the repeating unit of the formula in an amount of "ℓ".

Formalin Scavengers (S-1) to (S-6) and (S-12) to (S-23) are commercial products; and (S-7) to (S-11) can easily be produced by the method described in, for example, Bulletin of the Chemical Society of Japan, Vol. 39, pages 1559 to 1567, pages 1734 to 1738 (1966), Chemische der Berichte Vol 54b, pages 1802 to 1833, pages 2441 to 2479 (1921) and Beilstein Handbuch der Organischen Chemie HP 98 (1921). (S-24) and (S-25) can be produced by the method described in, for example, Beilstein handbuch der Organischen Chemie, 1st Add. Ed., Vol. 4, page 354, ibid., Vol, 3, page 63.

The formalin scavenger as mentioned above can be used in the form of a mixture of two or more thereof in the present invention.

The formalin scavenger of the present invention is incorporated in at least one of the silver halide emulsion layers, subbing layers, protective layers, interlayers, filter layers, anti-halation layers and other auxiliary layers which constitute the silver halide color photographic material of the present invention. The formalin scavenger may be incorporated into a magenta polymer coupler-containing silver halide emulsion layer the photographic properties of which would be deteriorated by contact with formaldehyde gas, or into a layer which is nearer to the support than the emulsion layer or a layer which is farther from the support than the emulsion layer, and in any case, the object of the present invention can be attained.

For incorporation of a formalin scavenger in the layer, a formalin scavenger as is may be added to a coating composition for forming the layer, or alternatively, a formalin scavenger is first dissolved in a solvent which would not adversely influence silver halide color photographic materials, for example, water or alcohols, in a proper concentration and the resulting solution may be added to the coating composition. Still alternatively, a formalin scavenger may also be dissolved in a high boiling point organic solvent and/or a low boiling point organic solvent and then dispersed in an aqueous solution by emulsification, and the resulting dispersion may also be added to the coating composition. The time for the addition of the formalin scavenger may be any time during the formation of the coating composition, but it is preferably added to the composition immediately before coating. The amount of the formalin scavenger to be added is suitably from 0.01 g to 10 g, preferably from 0.05 g to 5 g, per m^2 of the silver halide color photographic material.

When the photographic material of the present invention is a color photographic material, it may contain various anti-fading agents. Specific examples of anti-fading agents usable in the present invention include hindered phenols such as hydroquinoes, 6-hydroxychromans, 5-hydroxycoumarans, spirochromans, p-alkoxyphenols and bisphenols, and gallic acid derivatives, methylenedioxybenzenes, aminophenols, hindered amines as well as ether or ester derivatives formed by silylating or alkylating the phenolic hydroxyl group in these compounds. In addition, metal complexes such as (bissalicylaldoximato)/nickel complexes and (bis-N,N-dialkyldithiocarbamato)/nickel complexes may also be used.

For preventing the deterioration of yellow color images by heat, moisture and light, the compounds having both partial structures of hindered amine and hindered phenol moieties in one molecule described in U.S. Patent 4,268,593 may advantageously be used. In order to prevent the deterioration of magenta color images, especially by light, the spiroindanes described in JP-A-56-159644, and the hydroquinonediether or monoether-substituted chromans described in JP-A-55-09835 may give a good result. These compounds may be added to a light-sensitive layer by co-emulsifying than with the corresponding color coupler in an amount of, generally from 5 to 100 % by weight of the coupler, whereby the intended object can be attained. In order to prevent the deterioration of cyan color images by heat and especially by light, incorporation of an ultraviolet absorbent into both layers adjacent to the cyan-coloring layer is effective. In addition, an ultraviolet absorbent may also be added to a hydrophilic colloid layer such as a protective layer.

The photographic material of the present invention may contain a dye for anti-irradiation or anti-halation and may also contain an antistatic agent or a slide property-improving agent (friction reducing agent).

Specific examples of the additives are described in Research Disclosure No. 17643 (December, 1979) and No. 18716 (November, 1979).

The present invention may also be applied to a multi-layer and multi-color photographic material having at least two layers each having a different spectral sensitivity on a support. A multi-layer natural color photographic material generally has at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one blue-sensitive emulsion layer on a support. The order of these layers as arranged on the support may freely be selected. Preferred examples of the order for the layer constitution include red-sensitive layer, green-sensitive layer and blue-sensitive layer from the support; blue-sensitive layer, green-sensitive layer and red-sensitive layer from the support; blue-sensitive layer, red-sensitive layer and green-sensitive layer from the support; and green-sensitive layer, red-sensitive layer and blue-sensitive layer from the support. Each of the emulsion layers may contain two or more emulsion layer parts each having a different sensitivity degree; or a non-light-sensitive layer may be between two or more emulsion layers having the same sensitivity degree. It is typical that the red-sensitive emulsion layer contains a cyan-forming coupler, the green-sensitive emulsion layer contains a magenta-forming coupler and the blue-sensitive emulsion layer contains a yellow-forming coupler, but any other combinations may also be employed, as the case may be.

It is preferred that the photographic materials of the present invention have auxiliary layers such as a protective layer, and interlayer, a filter layer, an anti-halation layer and a white-reflective layer, if desired, in addition to the silver halide emulsion layers.

In the formation of the photographic materials of the present invention, the photographic emulsion layers and other layers are coated on a support which is generally used in conventional photographic materials, for example, a flexible support such as a plastic film, paper or cloth, or a rigid support such as glass, porcelain or metal. As examples useful as a flexible support, there are a film made of a semi-synthetic or synthetic polymer such as cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polystyrene, polyvinyl chloride, polyethylene terephthalate or polycarbonate, and a paper coated or laminated with a baryta layer or an α-olefin polymer (e.g., polyethylene, polypropylene or ethylene/ butene copolymer). The support may be colored with a dye or pigment. This may be blackened for the purpose of light-shielding. The rear surface of the support is generally coated with a emulsion layers and other layers. Before or after coating with the subbing layer, the surface of the support may be processed by glow discharge, corona discharge, ultraviolet irradiation or flame treatment.

For coating the silver halide photographic layers and other hydrophilic colloid layers on the support, various known coating methods, for example, dip coating, roller coating, curtain coating or extrusion coating, may be employed. If desired, plural layers may simultaneously be coated by the method described in U.S. Patents 2,681,294, 2,761,791, 3,526,528 and 3,508,947.

The color photographic materials of the present invention can be developed by the method described in the aforesaid Research Disclosure No. 17643, pages 28 to 29 and No. 18716, page 651, from left-hand column to right-hand column. The color photographic material of the present invention is generally rinsed with water or stabilized, after being developed and bleach-fixed or fixed.

Specifically, the color photographic material of the present invention is processed by a color negative-processing system (composed of color-developer bath, bleaching bath, fixation bath and stabilization bath) or by a color reversal-processing system (composed of black-and-white developer bath, reversal bath, color-developer bath, bleaching bath, fixation bath and stabilization bath). In particular, in the color reversal-processing system, the black-and-white developer bath desirably contains a developing agent containing a hydroquinone derivative and a phenidone derivative, and it is preferred that the bath further contains a silver halide solvent such as thiocyanate salt or a sulfite salt. In the reversal step, a foggant such as a tin salt may be used, and the reversal may be effected by light-irradiation.

When the photographic material of the present invention has a non-previously fogged internal latent image-type emulsion mentioned above, the material is imagewise exposed, and then, after or while the thus-exposed material is fogged by light or a nucleating agent, this is developed with a p-phenylenediamine color developing agent-containing surface developer and thereafter bleach-fixed to form a direct positive color image.

In particular, even though a low pH color developer having a pH value of 11.5 or lower is used, an excellent direct positive image can be obtained, and the photographic material of the present invention is advantageous in this point.

For the above-mentioned fogging treatment to be applied to the photographic material of the present invention, either a "photo-fogging method" in which a second exposure is applied to the whole surface of the light-sensitive layer of the material, or a "chemical fogging method" in which the material is developed in the presence of a nucleating agent may be employed. In addition, the material may also be developed in the presence of both a nucleating agent and light. Further, a nucleating agent may previously be incorporated into the photographic material, which may be fogged by exposure.

The details of the photo-fogging method are described in the Japanese Patent Application No. 61-226292, from page 33, line 17 to page 35, last line, and examples of nucleating agents which can be used in the present invention are also described therein from page 50, line 1 to page 53. In particular, the compounds of formulae (N-1) and (N-2) shown therein are preferred for use in the present invention.

Specific examples of compounds of formula (N-1) are as follows:

(N-I-1): 5-Ethoxy-2 methyl-1-propargylquinolinium Bromide
(N-I-2): 2,4-Dimethyl-propargylquinolinium Bromide
(N-I-3): 2-Methyl-1-{3-[2-(4-methylphenyl)hydrazono]butyl}-quinolinium Iodide
(N-I-4): 3,4-Dimethyl-dihydropyride[2,1-b]benzothiazolium Bromide

(N-I-5): 6-Ethoxythiocarbonylamino-2-methyl-1-propargylquinolinium Trifluoromethanesulfonate
(N-I-6): 2-Methyl-6-(3-phenylthioureido)-1-propargylquinolinium Bromide
(N-I-7): 6-(5-Benzotriazolcarboxamido)-2-methyl-1-propargylquinolinium Trifluoromethanesulfonate
(N-I-8): 6-[3-(2-mercaptoethyl)ureido]-2-methyl-1-propargylquinolinium Trifluoromethanesulfonate
(N-I-9): 6-{3-[3-(5-Mercapto-1,3,4-thiadiazol-2-ylthio)propyl]ureido}-2-methyl-1-propargylquinolinium Trifluoromethanesulfonate
(N-I-10): 6-(5-mercaptotetrazol-1-yl)-2-methyl-1-propargylquinolinium Iodide
(N-I-11): 1-Propargyl-2-(1-propenyl)quinolinium Trifluoromethanesulfonate
(N-I-12): 6-Ethoxythiocarbonylamido-2-(2-methyl-1-propenyl)-1-propargylquinolinium Trifluoromethanesulfonate
(N-I-13): 10-Propargyl-1,2,3,4-tetrahydroacridinium Trifluoromethanesulfonate
(N-I-14): 7-Ethoxythiocarbonylamino-10-propargyl-1,2,3,4-tetrahydroacridinium Trifluoromethanesulfonate
(N-I-15): 6-Ethoxythiocarbonylamino-1-propargyl-2,3-pentamethylenequinolinium Trifluoromethanesulfonate
(N-I-16): 7-[3-(5-Mercaptotetrazol-1-yl)benzamido]-10-propargyl-1,2,3,4-tetrahydroacridinium Perchlorate
(N-I-17): 6-[3-(5-mercaptotetrazol-1-yl)benzamido]-1-propargyl-2,3 pentamethylenequinolinium Bromide
(N-I-18): 7-(5-Mercaptotetrazol-1-yl)-9-methyl-10-propargyl-1,2,3,4-tetrahydroacridinium Bromide
(N-I-19): 7-[3-{N-[2-(5-mercapto-1,3,4-thiadiazol-2-yl)-thioethyl]carbamoyl}propanamido]-10-propargyl-1,2,3,4-tetrahydroacridinium Tetrafluoroborate
(N-I-20): 6-(5-mercaptotetrazol-1-yl)-4-methyl-1-propargyl-2,3-pentamethylenequinolinium Bromide
(N-I-21): 7-Ethoxythiocarbonylamino-10-propargyl-1,2-dihydroacridinium Trifluoromethanesulfonate
(N-I-22): 7-(5-Mercaptotetrazol-1-yl)-9-methyl-10-propargyl-1,2-dihydroacridinium Hexafluorophosphate
(N-I-23): 7-[3-(5-mercaptotetrazol-1-yl)benzamido]-10-propargyl-1,2-dihydroacridinium Bromide

Specific examples of the compounds of formula (N-II) are as follows:

(N-II-1): 1-Formyl-2 {4-[3-(2-methoxyphenyl)ureido}propyl]hydrazine
(N-II-2): 1-Formyl-2-{4-[3-{3-[3-(2,4-di-tert-pentylphenoxy)propyl]ureido}phenylsulfonylamino]phenyl}hydrazine
(N-II-3): 1-Formyl-2-{4-[3-(5-meroaptotetrazol-1-yl)benzamido}phenyl]hydrazine
(N-II-4): 1-Formyl-2-[4-{3-[3-(5-mercaptotetrazol-1-yl)phenyl]ureido}phenyl]hydrazine
(N-II-5): 1-Formyl-2-[4-{3-[N-(5-mercapto-4 methyl-1,2,4-triazol-3 yl)carbamoyl]propanamido}phenyl]hydrazine
(N-II-6): 1-Formyl-2-{4-[3-{N-[4-(3-mercapto-1,2,4-triazol-4-yl)phenyl]carbamoyl}propanamido]phenyl}hydrazine
(N-II-7): 1-Formyl-2-[4-{3-[N-(5-mercapto-1,3,4-thiadiazol-2-yl)carbamoyl]propanamido)phenyl]hydrazine
(N-II-8): 2-[4-benzotriazol-5-carboxamido)phenyl]-1-formylhydrazine
(N-II-9): 2-[4-{3-(N-benzotriazole-5-carboxamido)carbamoyl-propanamide]phenyl}-1-formylhydrazine
(N-II-10): 1-Formyl-2-{4-[1-(N-phenylcarbamoyl)thiosemicarbamido}phenyl]hydrazien
(N-II-11): 1-Formyl-2 {4-[3-(3-phenylthioureido)benzamido]phenyl}hydrazine
(N-II-12): 1-Formyl-2-[4-(3-hexylureido)phenyl]hydrazine
(N-II-13): 1-Formyl-2-{4-[3-(5-mercaptotetrazol-1-yl)benzenesulfonamido}phenyl)hydrazine
(N-II-14): 1-Formyl-2-{4-[3-{3-[3-(5-mercaptotetrazol-1-yl)phenyl]ureido}benzenesulfonamido]phenyl}hydrazine

As nucleation accelerators which can be used in the present invention, there are tetraazaindenes, triazaindenes and pentaazaindenes having at least one mercapto group which may optionally be substituted by an alkali metal atom or an ammonium group, as well as the compounds described in Japanese Patent Application No. 62-136948 (pages 2 to 6 and pages 16 to 43), Japanese Patent Application No. 62-136949 (pages 12 to 43) and Japanese Patent Application No. 62-15348 (pages 10 to 29).

Specific examples of nucleation accelerators which can be used in the present invention are as follows below, but present invention is not to be construed as being limited thereto:

(A-l): 3-Mercapto-1,2,4-triazolo[4,5-a]pyridine
(A-2): 3-Mercapto-1,2,4-triazolo[4,5-a]pyrimidine
(A-3): 5-Mercapto-1,2,4-triazolo[1,5-a]pyrimidine
(A-4): 7-(2-dimethylaminoethyl)-5-mercapto-1,2,5-triazolo[1,5-a]pyrimidine
(A-5): 3-Mercapto-7-methyl-1,2,4-triazolo[4,5-a]pyrimidine
(A-6): 3,6-Dimercapto-1,2,4-triazolo[4,5-b]pyridazine
(A-7): 2-Mercapto-5-methylthio-1,3,4-thiadiazole
(A-8): 3-Mercapto-4-methyl-1,2,4-triazole
(A-9): 2-(3-Dimethylaminopropylthio)-5-mercapto-1,3,4-thiadiazole Hydrochloride

(A-10): 2-(2-Morpholinoethylthio)-5-mercapto-1,3,4-thiadiazole Hydrochloride
(A-11): Sodium 2-Mercapto-5-methylthiomethylthio-1,3,4-thiadiazole
(A-12): 4-(2-Morpholinoethyl)-3-mercapto-1,2,4-triazole
(A-13): 2-[2-(2-dimethylaminoethylthio)ethylthio]-5-mercapto-1,3,4-thiadiazole Hydrochloride
(A-14): 2-(6-Dimethylaminohexylthio)-5-mercapto-1,3,4-thiadiazole Hydrochloride
(A-15): 2-{3-[2-Methyl-1-(1,4,5,6-tetrahydropyrimidinyl)]propylthio}-5-mercapto-1,3,4-thiadiazole Hydrochloride

Although the nucleation accelerator may be incorporated in the photographic material or in the processing solution, it is preferred to be incorporated into the photographic material, especially into the internal latent image-type silver halide emulsion or other hydrophilic colloid layers (e.g., en interlayer or protective layer) of the material. Especially preferably, it is incorporated into the silver halide emulsion layer or into the adjacent layers thereto in the phctographic material.

The amount of the nucleation accelerator to be added is preferably from 10^{-6} to 10^{-2} mol, especially preferably from 10^{-5} to 10^{-2} mol, per mol of the silver halide in the material.

When the nucleating accelerator is incorporated into the processing solution, i.e. the developer or a previous bath, thereto the amount thereof is preferably from 10^{-9} to 10^{-3} mol, especially preferably from 10^{-7} to 10^{-4} mol, per liter of the processing solution.

Two or more kinds of nucleation accelerators can be used in mixture.

When the photographic material of the present invention is used in a color diffusion transfer process, a color developing agent can be used as the coloring agent. It is advantageous that a coloring agent which itself is alkaline (in a developer) or is non-diffusive (or immobile) but which may release a diffusive dye (or a precursor thereof) as a result of development is used in this process. As the diffusive dye-releasing coloring agent (DRR compound), there are couplers or redox compounds which may release a diffusible dye. these are useful not only for the color diffusion transfer process (wet type) but also for heat-developing photographic materials (dry type) as described in, for example, JP-A-58-58543.

The diffusible dye-releasing redox compounds (hereinafter referred to as "DRR compounds") can be represented by the following general formula:

(Ballast)———(Redox-cleaving Atomic Group)——— D

In the formula, (Ballast) and (Redox-cleaving Atomic Group) may be those derived from the compounds described in JP A-58-163938, pages 12 to 22. D represents a dye (or precursor thereof) moiety. The dye moiety may be bonded to the (Redox-cleaving Atomic Group) via a linking group. As the dye moiety for D, the dyes described in the following publications are advantageously used.

Examples of Yellow Dyes:

The dyes described in U.S.Patents 3,597,200, 3,309,199, 4,013,633, 4,245,028, 4,156,609, 4,139,383, 4,195,992, 4,145,641, 4,148,643 and 4,336,322; JP-A-51-114930 and 56-71072 and Research Disclosure Nos. 17630 (1978) and 16475 (1977) are preferred.

Examples of Magenta Dyes:

The dyes described in U.S. Patents 3,453,107, 3,544,545, 3,932,380, 3,931,144, 3,932,308, 3,954,476, 4,233,237, 4,255,509, 4,250,246, 4,142,891, 4,207,104 and 4,287,292; JP-A-52-106727, 53-23628, 55-36804, 56-73057, 56-71060 and 55-134 are preferred.

Examples of Cyan Dyes:

The dyes described in U.S. Patents 3,482,972, 3,939,760, 4,013,635, 4,268,625, 4,171,220, 4,242,435, 4,142,891, 4,195,994, 4,147,544 and 4,148,642; British Patent 1,551,138; JP-A-54 99431, 52-8827, 53-47823, 53-143323, 54-99431 and 56-71061; European Patents (EPC) 53037 and 53040; and research disclosure Nos. 17630 (1978) and 16475 (1977) are preferred.

The amount of the dye compound to be coated is generally from about 1×10^{-4} to 1×10^{-2} mol/m², preferably from 2×10^{-4} to 2×10^{-2} mol/m².

In the photographic material of the present invention, the coloring agent can be incorporated into the corresponding silver halide emulsion layer or into the adjacent layers thereof in the side to be exposed or in the opposite side thereof.

When the photographic material of the present invention is used in a color diffusion transfer process, the photographic emulsion may be coated on the same support having an receiving layer, as integrated with the layer, or alternatively, it may be coated on a different support. The silver halide photographic emulsion layer (light-sensitive element) and the image-receiving layer (image-receiving element) may be combined to provide a combined film unit, or these may be provided independently in the form of the respective separate photographic material units. Regarding the combined film unit type, it may be either a completely integrated type for exposure, development and formation of reversal images where the images formed may directly be seen or a semi-integrated type for exposure and development where the developed sheet is released to see the image formed. The latter type is preferred for the present invention.

The present invention can be applied to various kinds of photographic materials.

For example, these include black-and white negative films, reversal films, color negative films for general use or for movie films, color reversal films for slides or television use, color reversal papers and instant color films, as typical examples. In addition, the present invention may also be applied to color hard copies for preservation of images from full color duplicators or CRT. Further, the present invention can be applied to black-and-white photographic materials for three color coupler mixture described in Research Disclosure No. 17123 (July, 1978).

The color developer to be used for development of the photographic materials of the present invention is preferably an alkaline aqueous solution consisting mainly of an aromatic primary amine color developing agent. As the color developing agent, p-phenylenediamine compounds are preferably used although aminophenol compounds are also useful. Specific examples of the compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline and sulfates, hydrochlorides and p-toluenesulfonates thereof. These compounds can be used in the form of a mixture of two or more of them, in accordance with the object thereof.

The color developer generally contains a pH buffer such as alkali metal carbonates, borates or phosphates, as well as a development inhibitor or an anti-foggant such as bromides, iodides, benzimidazoles, benzothiazoles or mercapto compounds. In addition, it may further contain a preservative of various kinds, such as hydroxylamine, diethylhydroxylamine, sulfites, hydrazines, phenylsemicarbazides, triethanolamine, catecholsulfonic acids and triethylenediamines (1,4-diaza-bicyclo[2,2,2]octane); an organic solvent, such as ethylene glycol and diethylene glycol; a development accelerator, such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts and amines; a dye-forming coupler; a competing coupler; a fogging agent such as sodium boronhydride; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a tackifier; and a chelating agent of various kinds, such as aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, if desired. As the chelating agents usable in the present invention, there may be mentioned ethylenediaminetetraacetic acid, nitrilo-triacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediamine-tetraacetic acid, hydroxyethylimino-diacetic acid , 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N′,N′- tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid) and salts thereof, as typical examples.

The color developer generally has a pH value of from 9 to 12. The amount of the replenisher for the developer, although depending upon the kind of the color photographic material to be processed, is generally one liter of less per m^2 of the material being processed, and the amount may be reduced to 300 ml or less if the bromide ion concentration in the replenisher is lowered. When the amount of the replenisher is reduced, it is preferred to reduce the contact area between the processing bath and air so as to prevent the evaporation and aerial oxidation of the processing solution. In addition, the amount of the replenisher may be reduced by means of inhibiting the accumulation of the bromide ion in the developer.

After color development, the photographic emulsion layer thus processed is generally bleached. Bleaching may be carried out simultaneously with fixation (for bleach-fixing step),or may be carried out separately therefrom. In order to accelerate the photographic processing, bleaching may be followed by bleach-fixation. In addition, other various modifications, for example, bleach-fixation in continuous two bleach-fixing bathes, fixation prior to bleach-fixation, or bleach-fixation followed by bleaching, may also be employed in accordance with the object of the photographic processing. As the bleaching agent can be used, for example, compounds of poly-valent metals such as iron(III), cobalt(III), chromium(VI) or copper(II), as well as peracids, quinones and nitro compounds. Specific examples of the bleaching agents include ferricyanides; bichromates; organic complexes with iron(III) or cobalt(III), for example, complexes with an aminopolycarboxylic acid such as ethylenediamine-tetraacetic acid, diethylenetriaminepentaacetic acid, cyclo-hexanediamine-tetraacetic acid, methylimino diacetic acid, 1,3-diaminopropane-tetraacetic acid or glycoletherdiamine tetraacetic acid, or an organic acid such as citric acid, tartaric acid or malic acid; persulfates; bromates; permanganates; and nitrobenzenes. Among them, aminopolycarboxylic acid/iron(III) complexes such as ethylenediamine-tetraacetic acid/iron(III) complex as well as persulfates are preferred from the viewpoint of rapid processability and prevention of environmental pollution. Aminopolycarboxylic acid/iron(III) complexes are especially useful both in a bleaching solution or in a bleach-fixing solution. The pH value of the bleaching solution or bleach-fixing solution containing the said aminopolycarboxylic acid/iron(III) complex is generally from 5.5 to 8, but the solution may have a lower pH value so as to accelerate the processing with the solution.

The bleaching solution, bleach-fixing solution and the previous bath thereof may contain a bleaching accelerator, if desired. As examples of usable bleaching accelerators, there may be mentioned the mercapto group- or disulfido bond-containing compounds described in U.S. Patents 3,893,858, West German Patent 1,290,812, JP-A-53-95630 and Research Disclosure No. 17129 (July, 1978); the thiazolidine derivatives described in JP-A-50-140129; the thiourea derivatives described in U.S. Patent 3,706,561; the iodides described in JP-A-58-16235; the polyoxyethylene compounds described in West German Patent 2,748,430; the polyamine compounds described in JP-B-45-8836; and bromide ions. Among them,the mercapto group- or disulfido group-containing compounds are preferred as having a large accelerating activity, and in particular, the compounds described in U.S. Patent 3,893,858, West Germany Patent 1,290,812 and JP-A-53-95630/78 are preferred. Further, the compounds described in U.S. Patent 4,552,834 are also preferred. The bleaching accelerator can be incorporated into the photographic materials of the present invention. When picture-taking color photographic materials are beleach-fixed, the bleaching accelerators are especially advantageous.

As the fixing agent, there are thiosulfates, thiocyanates, thioether compounds, thioureas and a large amount of iodides. Use of thiosulfates is general, and in particular, ammonium thiosulfate is used most widely. As the preservative for the bleach-fixing solution, sulfites, bisulfites or carbonyl-bisulfite adducts are preferred.

The silver halide color photographic materials of the present invention are, after being desilvered, generally subjected to rinsing in water and/or stabilization. The amount of the rinsing water may be determined within a broad range in accordance with the characteristic of the photographic material to be processed (for example, couplers and other constitutional components), the use of the material, as well as the temperature of the rising water, the number (stage number) of rinsing tanks, the kind of replenishment system (counter current or normal current) and other various conditions. Among these conditions, the relation between the number of the rinsing tanks and the amount of the rinsing water may be determined by the method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64,pages 248 to 253, (May, 1955).

In accordance with the multi-stage counter current system described in this publication, although the amount of the rinsing water could be reduced noticeably, there are problems that bacteria remarkably propagate because of the increase of the residence time of water in the rinsing tanks, and floating substances formed adhere to the photographic material processed. In the processing of the color photographic materials of the present invention, the method of decreasing the amount of the calcium ion and magnesium ion in the rinsing water described in Japanese Patent Application No. 62-131632 can effectively be used to overcome these problems. In addition, the isothiazolone compounds and thiabendazoles described in JP-A-57-8542 as well as chlorine germicides, such as sodium chloroisocyanurate and other benzotriazoles, and the germicides described in H. Horiguchi, Chemistry of Bactericidal and Fungicidal Agents; Bactericidal and Fungicidal Techniques against Microorganisms (edited by Sanitary Technical Association, Japan); and Handbook of Bactericidal and Fungicidal Agents (edited by Japan Bactericidal and Fungicidal Association) may also be used.

In the processing of the photographic materials of the present invention, the pH value of the rinsing water is from 4 to 9, preferably from 5 to 8. The temperature of the rinsing water and the rinsing time may also be determined variously within a broad range, in accordance with the characteristics of the photographic material to be processed and the use thereof, and in general, the range of from 15 °C to 45 °C and from 20 seconds to 10 minutes, preferably from 25 °C to 40 °C and from 30 seconds to 5 minutes, may be selected. In place of the above-mentioned rinsing-in-water step, the photographic material of the present invention may be processed directly by a stabilizing solution. In such a stabilization step, all the known methods described in JP-A-8543, 58-14834 and 60-220345 can be utilized.

The stabilizing bath for the stabilization step may also contain various kinds of chelating agents and fungicides. The overflow solution resulting from the replenishment of the rinsing bath and/or stabilizing bath may be re-used in the previous desilvering step or in other steps.

The silver halide color photographic materials of the present invention can contain a color developing agent therein for the purpose of simplifying and accelerating the processing of the materials. For incorporation of a color developing agent into the materials, a precursor of the color developing agent is preferably used. As precursors, for example, there may be mentioned the indoaniline compounds described in U.S. Patent 3,342,597, the Shiff base compounds described in U.S. Patent 3,342,599 and research Disclosure Nos. 14850 and 15159, the aldol compounds described in Research Disclosure No. 13924, the metal complexes described in U.S. Patent 3,719,492 and the urethane compounds described in JP-A-53-135628.

The silver halide color photographic materials of the present invention may contain various kinds of 1-phenyl-3-pyrazolidones, if desired, for the purpose of accelerating color development. Specific examples of the development accelerating compounds are described in JP-A-56-64339, 57-144547 and 58-115438.

The respective processing solutions for the photographic materials of the present invention are used at from 10°C to 50°C. In general, the processing temperature may be increased so as to accelerate the processing step and shorten the processing time, or on the contrary, the processing temperature may be made lower so as to improve the quality of the image formed and to improve the stability of the processing solution. In addition, for the purpose of reducing silver in the photographic materials, processing by cobalt intensification or hydrogen peroxide intensification described in West German Patent 2,226,770 and U.S. Patent 3,674,499 may also be employed.

Regarding the amount of the replenisher to be replenished to the respective processing steps, the less used, the better. Specifically, the amount of the replenisher is preferably from 0.1 to 50 times, more preferably from 3 to 30 times, the amount of the solution of the previous bath as brought into the bath from the previous bath together with the photographic material being processed, per unit area of the material.

When the photographic materials of the present invention are black-and-white photographic materials, these may be developed with various kinds of known developing agents. For example, polyhydroxybenzenes such as hydroquinone, 2-chlorohydroquinone, 2-methylhydroquinone, catechol or pyrogallol; aminophenols such as p-aminophenol, N-methyl-p-aminophenol or 2,4-dieminophenol; 3-pyrazolidones such as 1-phenyl-3-pyrazolidones, 1-phenyl-4,4′-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidones or 5,5-dimethyl-1-phenyl 3-pyrazolidone; as well as ascorbic acids can be used, alone or in a combination thereof. In addition, the developers described in JP-A-58-55928 may be used. The developer may be incorporated into an alkaline processing composition (processing element) or into a pertinent layer in the light-sensitive element.

The developer may contain a preservative such as sodium sulfite, potassium sulfite, ascorbic acid or reductones (e.g., piperidinohexose-reductone), if desired.

The internal latent image-type emulsion-containing photographic material of the present invention can be developed with a surface developer to obtain a direct positive image. The surface developer is such that the development therewith is induced substantially by the latent image or fog nuclei existing on the surface of silver halide grains. Although the surface developer preferably does not contain a silver halide-solubilizer, it may contain the solubilizer (for example, sulfites) provided that the solubilizer does not substantially participate in the internal latent image before the completion of the development of the silver halide grains by the surface development center.

The developer may contain an alkaline agent and, as a buffer, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, trisodium phosphate or sodium metaborate. The content of the these agents in the developer may be selected so that the pH value of the resulting developer falls within the range of from 9 to 13, preferably from 10 to 11.2.

It is advantageous that the developer contains a compound which is generally used as an antifoggant, such as a benzimidazole (e.g., 5-nitrobenzimidazole), a benzotriazole (e.g., benzotriazole or 5-methylbenzotriazole) or the like, so as to further lower the minimum density of the direct positive image to be formed.

The details of developing agent, preservatives and buffers for black-and-white photographic materials as well as specific examples of the developing method of the materials and the use of the materials are described in Research Disclosure No. 17643 (December, 1978), XIX to XXI.

In accordance with the present invention, when the compounds of the above-mentioned formulae (1) and (2) are used, the above-mentioned aromatic primary amine developing agents are preferably used.

When the compounds of the above-mentioned formula (3) are used, any and every silver halide developing agent (or electron-donating agent) can be used provided that it may react with the compound of formula (3) by cross-oxidation.

The developing agent can be incorporated into an alkaline development-processing solution (processing element) or may also be incorporated into a pertinent layer of the photographic element. Examples of the developing agents which may be used in the present invention include hydroquinones and aminophenols, such as N-methylaminophenol, 1-phenyl-3-pyrazolidinone, 1-phenyl-4,4-dimethyl-3-pyrazolidinone, 1-

phenyl-4-methyl-4- oxymethyl-3 pyrazolidinone, 1-phenyl-4-methyl-4-oxymethyl-3-pyrazolidinone, N,N-diethyl-p-phenylenediamine, 3-methyl-N,N-diethyl-p-phenylenediamine, and 3-methoxy N-ethoxy-p-phenylenediamine.

Among those mentioned above, black-and-white developing agents which capable of reducing stains in an image-receiving layer (mordant layer) are especially preferred for same reason as in the case of the aforesaid alkaline development-processing solution.

When the photographic materials of the present invention are used as film units for diffusion transfer process, these are preferred to be processed with a viscous developer. The viscous developer is a liquid composition containing components necessary for development of silver halide emulsions (and formation of diffusion-transferred color images), and the main component of the solvent is water, which may often contain any other hydrophilic solvent such as methanol or methyl cellosolve. Preferably, the processing composition contains a hydrophilic polymer, such as a macromolecular polyvinyl alcohol, hydroxyethyl cellulose or sodium carboxymethyl cellulose. It is convenient that the polymer is added to the composition in such an amount to give a viscosity of 1 poise or more, preferably from 500 to 1000 poises or so, at room temperature to the processing composition.

The above-mentioned processing composition is preferably put in a container capable of being broken under pressure, for example, as described in U.S. Patents 2,543,181, 2,643,886, 2,653,732, 2,723,051, 3,056,491, 3,056,492 and 3,152,515.

The following examples are provided to further illustrate the present invention, but are not to be construed as limiting the present invention in any way.

Unless otherwise indicated, all parts, percents and ratios are by weight.

EXAMPLE 1

Preparation of Emulsion (A):

500 ml of an aqueous 26% potassium bromide solution and 500 ml of an aqueous 34% silver nitrate solution were simultaneously added to an aqueous 3% gelatin solution to which 3,4-diemthyl-1,3-thiazoline-2-thione had been added in an amount of 0.3 g per mol of Ag,with vigorous stirring, at 75 °C over a period of about 20 minutes to prepare an octahedral monodisperse silver bromide emulsion having a mean grain size of 0.4 µm. To the emulsion were added sodium thiosulfate and chloroauric acid (tetra-hydrate) each in an amount of 6 mg per mol of Ag, and the whole was heated at 75 °C for 80 minutes for chemical sensitization. The thus-obtained silver bromide grains, as cores, were grown for a further 40 minutes under the same sedimentation conditions as in the first step to finally obtain an octahedral monodisperse core/shall silver bromide emulsion having a mean grain size of 0.7 µm. After washing with water and desalting, sodium thiosulfate and chloroauric acid (tetrahydrate) were added to the emulsion each in an amount of 1.5 mg per mol of Ag and heated for 60 minutes at 60 °C for chemical sensitization to obtain an internal latent image-type silver halide emulsion (A). The fluctuation coefficient of the grain size distribution was 10%.

Preparation of Emulsion (B):

30 g of gelatin was added to one liter of a mixed solution containing 0.5 mol/liter of KBr, 0.2 mol/liter of NaCl and 0.0015 mol/liter of KI and dissolved, and then 700 cc of a solution containing 1 mol/liter of silver nitrate was added to the resulting solution at 60 °C over a period of 20 minutes. Then this was physically ripened for 20 minutes.

After the soluble halides were removed by washing with water, 20 g of gelatin was added and then water was added to make a 1200 cc emulsion. Thus a silver halide emulsion having a mean grain size of 0.4 µm was obtained.

500 cc of an aqueous silver nitrate (1 mol/liter) solution and 500 cc of an aqueous sodium chloride (2 mol/liter) solution were simultaneously added to 300 cc of the emulsion at 60 °C to precipitate a silver chloride shell over the cores. After washing with water, a silver halide emulsion (B) having a mean grain size of 0.7 µm was obtained.

Preparation of Photographic Paper Samples:

The core/shell type internal latent image emulsion (A) was used, and the layers having the compositions mentioned below were coated on a paper support both surfaces of which had been laminated with polyethylene, to prepare a multi-layer color photographic paper.

The coating compositions were prepared as described below.

Preparation of Coating Composition for First Layer:

10 ml of ethyl acetate and 4 ml of Solvent (c) were added to 10 g of the Cyan Coupler (a) and 2.3 g of the Color Image Stabilizer (b) and dissolved, and the resulting solution was dispersed by emulsification in 90 ml of an aqueous 10% gelatin solution containing 5 ml of 10% sodium dodecylbenzenesulfonate. Separately the following red-sensitizing dye was added to the above-mentioned silver halide emulsion (containing 70 g/kg of Ag) in an amount of 2.0×10^{-4} mol per mol of the silver halide to obtain 90 g of a red-sensitive emulsion. The emulsified dispersion A, the red-sensitive emulsion and Development Accelerator (d) were mixed and dissolved, and the gelatin was added thereto to obtain a coating composition for the first layer. the contents of the respective components in the composition are shown below.

Other coating compositions for the second to seventh layers and B1 and B2 layers were also prepared in the same manner as the preparation of the coating composition for the first layer. As a gelatin hardening agent for each layer, sodium 1-oxy-3,5-dichloro-s-triazine and 1,2-bis(vinylsulfonylacetamido)-ethane were used, each in an amount of 0.6% by weight. In addition, the compound of the present invention was added in an amount of 1.0×10^{-4} mol per mol of Ag, as indicated in Table 1 below, or in an amount of 5.0 x 10-3 mol per mol of Ag, as indicated in Table 2 below.

Seventh Layer: Protective Layer

Gelatin	1.33 g/m^2
Latex Grains of Polymethyl Acrylate (mean grain size 2.7 μm)	0.05 g/m^2
Acryl-modified Polyvinyl Alcohol Copolymer (modification degree 17%)	0.17 g/m^2

Sixth layer: Ultraviolet Absorbing Layer

Gelatin	0.54 g/m^2
Ultraviolet Absorbent (i)	5.10×10^{-4} mol/m^2
Solvent (k)	0.08 g/m^2

Fifth Layer: Blue-sensitive Emulsion Layer

Emulsion	0.40 g/m^2 as Ag
Gelatin	1.35 g/m^2
Yellow Coupler (1)	6.91 x 10-4 mol/m^2
Color Image Stabilizer (m)	0.13 g/m^2
Solvent (h)	0.02 g/m^2
Development Accelerator (d)	32 g/m^2

Fourth Layer: Ultraviolet Absorbing Layer

Gelatin 1.60 g/m^2
Colloidal Silver 0.10 g/m^2
Ultraviolet Absorbent (i) 1.70 x 10^{-4} mol/m^2
Color Mixing Preventing Agent (j) 1.60 x 10^{-4} mol/m^2
Solvent (k) 0.24 g/m^2

Third Layer: Green-sensitive Emulsion Layer

Emulsion 0.18 g/m^2 as Ag
Gelatin 1.36 g/m^2
Magenta Coupler (f) 4.60 x 10^{-4} mol/liter
Color Image Stabilizer (g) 0.14 g/m^2
Solvent (h) 0.42 g/m^2
Development Accelerator (d) 32 mg/m^2

Second Layer: Color Mixing Preventing Layer

Gelatin 0.90 g/m^2
Colloidal Silver 0.02 g/m^2
Color Mixing Preventing Agent (e) 2.33 x 10^{-4} mol/m^2

First Layer: Red-sensitive Emulsion Layer

Emulsion 0.39 g/m^2 as Aq
Gelatin 0.90 g/m^2
Cyan Coupler (a) 7.05 x 10^{-4} mol/m^2
Color Image Stabilizer (b) 5.20 x 10^{-4} mol/m^2
Solvent (c) 0.22 g/m^2
Development Accelerator (d) 32 mg/m^2

Support:

Polyethylene-laminated paper (containing 4 g/m^2 of white pigment (TiO_2)and 18 g/m^2 a bluish dye (ultramarine) in the polyethylene layer on the side of the first layer, having a thickness of 105 µm.

B1 Layer: (Back layer opposite to the emulsion layers):

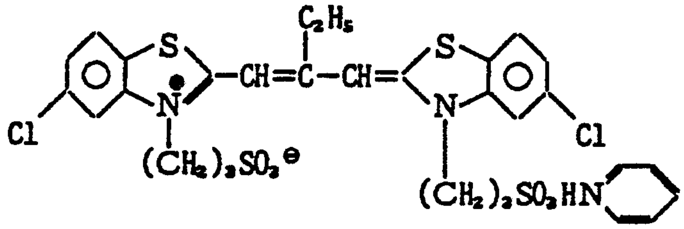
Gelatin 2.7 g/m^2

B2 Layer: (Back layer opposite to the emulsion layers):

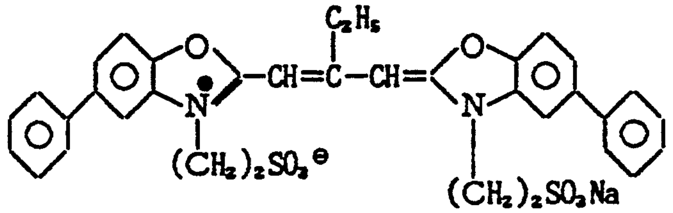
Gelatin 1.0 g/m^2
Latex grains of polymethyl acrylate (mean grain size 3.5 µm) 0.09 g/m^2

The following compounds were used as the respective spectral sensitizing dyes.

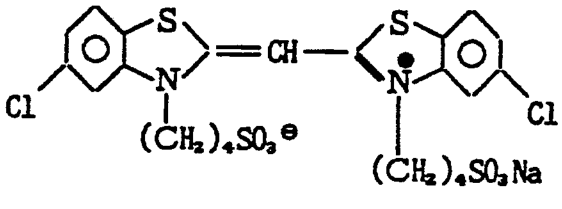
Red-sensitive Emulsion Layer Dye:



Green-sensitive Emulsion Layer:

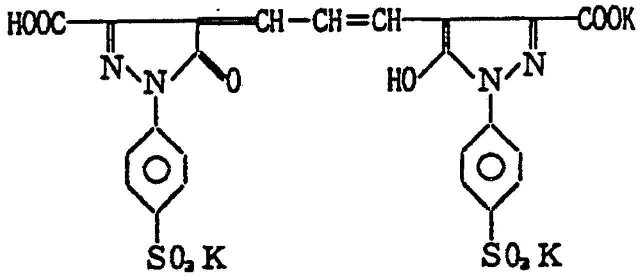


Blue-sensitive Emulsion Layer:

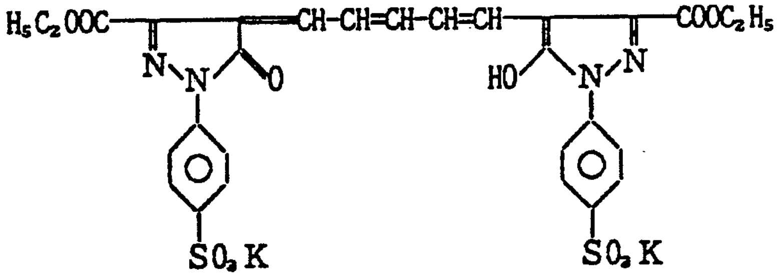


The following anti-irradiation dyes were used.

Anti-irradiation Dye for Green-sensitive Emulsion Layer:



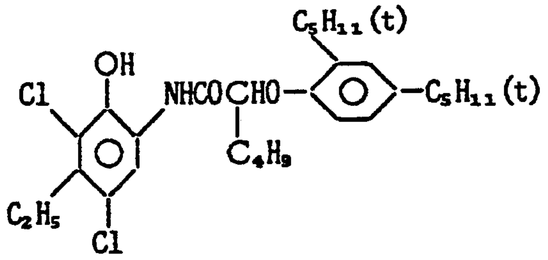
Anti-irradiation Dye for Red-sensitive Emulsion Layer:



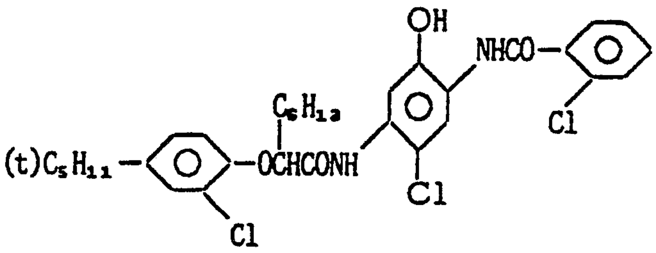
The couplers and other compounds used above had the following structural formulae:

Cyan Coupler (a):

Mixture (1/1, by mol) of the following compounds

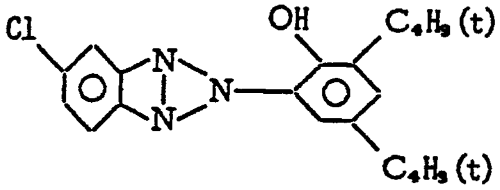


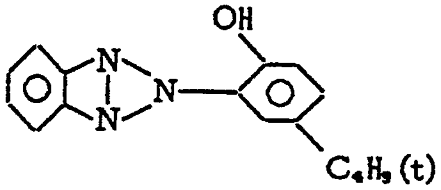
and



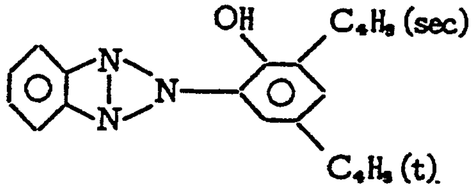
Color Image Stabilizer (b):

Mixture (1/3/3, by mol) of the following compounds

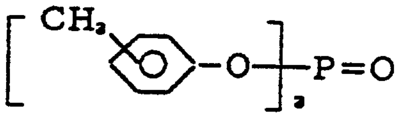




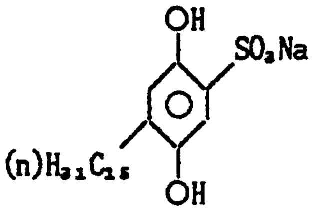
and



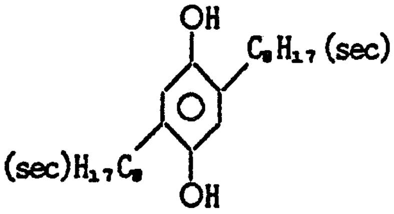
Solvent (c):



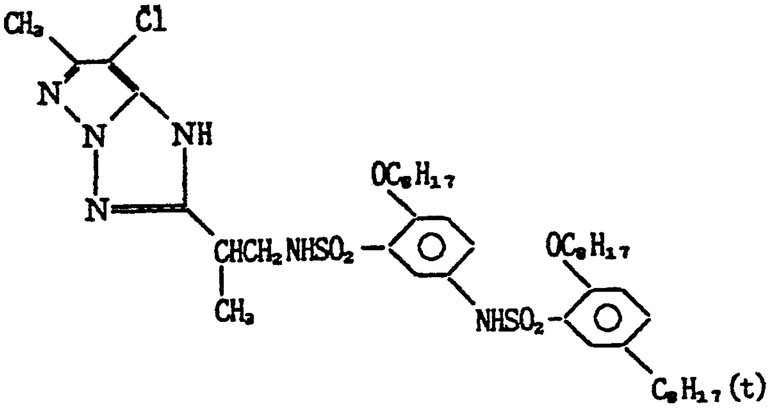
Development Accelerator (d):



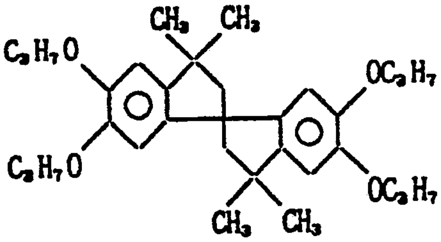
Color Mixing Preventing Agent (e):



Magenta Coupler (f):



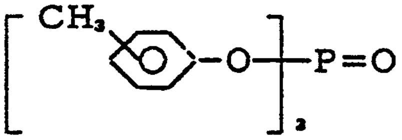
Color Images Stabilizer (g):



Solvent (h):

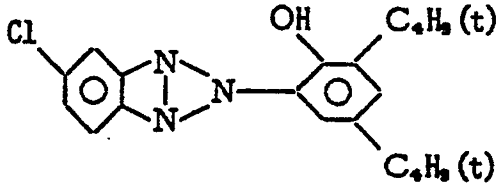
Mixture (2/1, by weight) of the following compounds

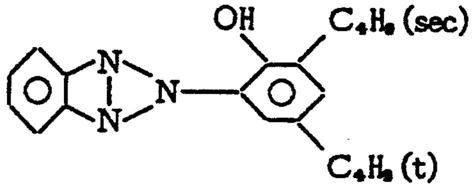
$\left[(n)C_8H_{17}O\right]_3P=O$ and



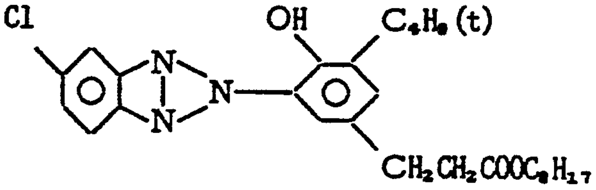
Ultraviolet Absorbent (i):

Mixture (1/5/3, by mol) of the following compounds

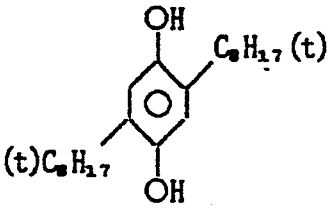




and



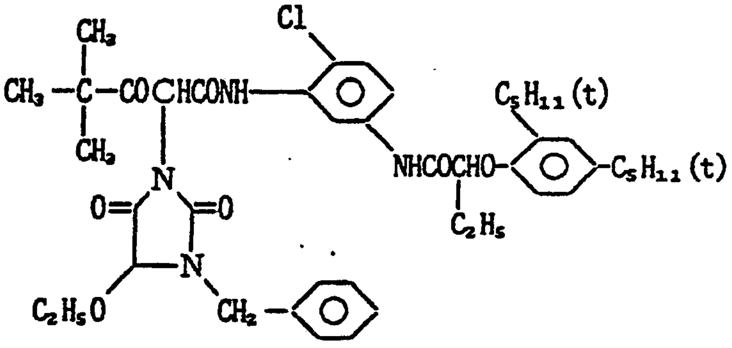
Color Mixing Preventing Agent (j):



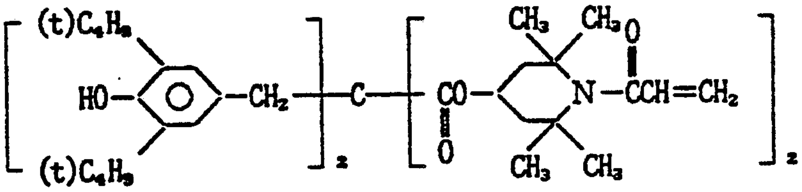
Solvent (k):

$$\left[\text{iso}C_9H_{19}O\right]_3 P=O$$

Yellow Coupler (1):



Color Image Stabilizer (m):



The thus-prepared color photographic paper was wedgewise exposed (1/10 sec, 10 CMS) and then processed in accordance with process (A) mentioned below. Then, the density of the magenta color image formed was measured. 15 seconds after the initiation of the development, fog exposure was effected for a period of 10 seconds (0.5 lux on the surface of the photographic material film processed, with color temperature of 5400° K).

The results obtained were shown in Table 1 below.

Process (a)	Time	Temperature
Color Development	1 min 50 sec	37° C
Bleach-fixation	40 sec	37° C
Stabilization (1)	20 sec	37° C
Stabilization (2)	20 sec	37° C
Stabilization (3)	20 sec	37° C

The replenishment system for the stabilizing step was a counter current replenishment system in which a replenisher was added to the last stabilizing bath (3), and the overflow solution from the stabilizing bath (3) was introduced into the previous stabilizing bath (2), and the overflow solution from the stabilizing bath (2) was also introduced into the previous stabilizing bath (1).

The processing solutions used in the process (A) were as follows:

Color Developer

	Solution
Diethylenetriamine-pentaacetic Acid	2.0 g
Benzyl Alcohol	12.8 g
Diethylene Glycol	3.4 g
Sodium Sulfite	2.0 g
Sodium Bromide	0.26 g
Hydroxylamine Sulfate	2.60 g
Sodium Chloride	3.20 g
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline	4.25 g
Potassium Carbonate	30.0 g
Brightening Agent (Stilbene-type)	1.0 g
Water to make	1000 ml
pH	10.20
(pH was adjusted by potassium hydroxide or hydrochloric acid.)	

Bleach-Fixing Solution:

	Solution
Ammonium Thiosulfate	110 g
Sodium Hydrogen Sulfite	10 g
Diethylenetriamine-pentaacetic Acid Iron(III) Ammonium Monohydrate	56 g
Ethylenediamine-tetraacetic Acid Disodium Dihydrate	5 g
2-Mercepto-1,3,4-triazole	0.5 g
Water to make	1000 ml
pH	6.5
(pH was adjusted by aqueous ammonia or hydrochloric acid.)	

	Solution
1-Hydroxyethylidene-1,1′-diphosphonic Acid (60%)	1.6 g
Bismuth Chloride	0.35 g
Polyvinyl Pyrrolidone	0.25 g
Aqueous Ammonia	2.5 ml
Trisodium Nitrilotriacetate	1.0 g
5-Chloro-2-methyl-4-isothiazolin-3-one	50 mg
2-Octyl-4-isothiazolin-3-one	50 mg
Brightening Agent (4,4′-Dieminostilbene type)	1.0 g
Water to make	1000 ml
pH	7.5
(pH was adjusted by potassium hydroxide or hydrochloric acid.)	

In the preparation of color photographic paper samples, the compound of the present invention or Comparative Compound (A) or (B) was added to the third layer in an amount of 1.0 x 10^{-4} mol per mol of

Ag, as indicated in Table 1 below.

The thus prepared photographic paper samples were incubated in an atmosphere of 40° C and 80 %RH for 3 days and then exposed and processed in the same manner as mentioned above. Then the magenta density of the image formed in each sample was measured, and the results obtained were shown in Table 1.

Table 1

No.	Compound Added	Incubation				Note
		No		Yes		
		Dmax	Dmin	Dmax	Dmin	
101	None	2.0	0.10	1.2	0.14	Control
102	Comparative Compound (A)	2.0	0.10	1.5	0.10	Comparison
103	Comparative Compound (B)	2.1	0.10	2.0	0.10	"
104	1-1	2.4	0.10	2.3	0.10	The Invention
105	1-2	2.4	0.10	2.3	0.10	"
106	1-6	2.3	0.10	2.2	0.10	"
107	1-18	2.4	0.10	2.2	0.10	"
108	2-1	2.2	0.10	2.1	0.10	"
109	3-1	2.3	0.10	2.2	0.10	"
110	3-7	2.5	0.10	2.4	0.10	"
111	3-8	2.5	0.10	2.4	0.10	"

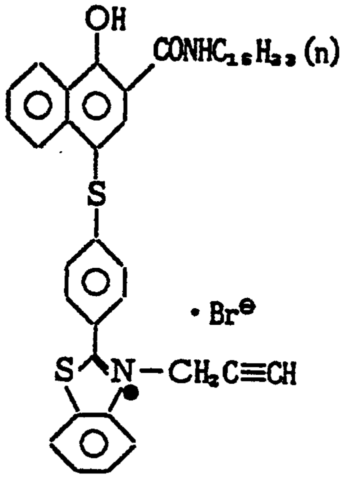
When not incubated, the maximum image density of Samples Nos. 104 to 111, each having the compound of the present invention, was larger than that of Sample No. 101 (having no compound for control) and Sample No. 102 (having Comparative Compound A) and Sample No. 103 (having Comparative Compound B). As compared with the control Sample No. 101, both the decrease of the maximum image density (Dmax) and the increase of the minimum image density (Dmin) because of incubation were smaller in the samples having the compound of the present invention.

Next, the compound of the present invention (1-1, 1-3, 1-4, 1-9, 1-15, 2-2, 3-1, 3-4, 3-8 or 3-10) was added to the first layer and color photographic paper samples were prepared in the same manner as the preparation of the Sample No. 101. These samples were incubated under the same conditions as above and then exposed and developed (also in the same manner as above) and the same results were obtained.

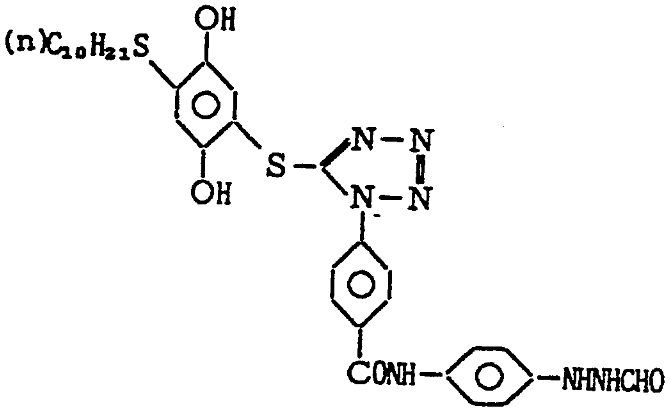
The compound of the present invention (1-1, 1-3, 1-5, 1-10, 3-2, 3-8, 3-9 or 3-14) wad added to the fifth layer and color photographic paper samples were prepared, also in the same manner as above. The same results were also obtained.

From the above results, it is clear that not only the maximum image density increases but also the storage stability was improved in direct positive color photographic materials by the addition of the compounds of the present invention.

Comparative Compound (A): (described in JP-A-59-157638



Comparative Compound (B): (described in JP-A-60-107029



In preparation of color photographic samples, the compound of the present invention or Comparative Compound (A′) or (B) was added to the third layer in an amount of 5.0 x 10^{-3} mol per mol of Ag, as indicated in Table 2 below.

The thus prepared photographic paper samples were incubated in an atmosphere of 40 °C and 80% RH for 3 days and then exposed and processed in the same manner as mentioned above. Then the magenta density of the image formed in each sample was measured, and the results obtained were shown in Table 2.

Table 2

No.	Compound Added	Incubation				Note
		No		Yes		
		Dmax	Dmin	Dmax	Dmin	
101	None	2.0	0.10	1.2	0.14	Control
102′	Comparative Compound (A′)	2.1	0.10	2.0	0.10	Comparison
103	Comparative Compound (B)	2.1	0.10	2.0	0.10	"
112	4-1	2.4	0.10	2.3	0.10	The Invention
113	4-2	2.4	0.10	2.3	0.10	"
114	4-8	2.3	0.10	2.2	0.10	"
115	4-11	2.3	0.10	2.2	0.10	"
116	5-1	2.2	0.10	2.1	0.10	"
117	6-8	2.5	0.10	2.4	0.10	"
118	6-9	2.5	0.10	2.5	0.10	"
119	6-10	2.4	0.10	2.4	0.10	"

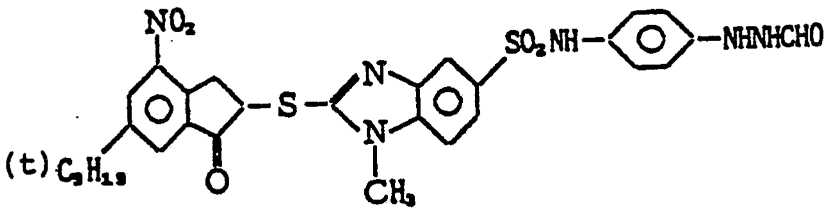
When not incubated, the maximum image density of Samples Nos. 112 to 119, each having the compound of the present invention, was larger than that of Sample No. 101 (having no compound for control), Sample No. 102′ (having Comparative Compound A′) and Sample No. 103 (having Comparative Compound B). As compared with control Sample No. 101, both the decrease of the maximum image density (Dmax) and the increase of the minimum image density (Dmin) because of incubation were smaller in the samples containing the compound of the present invention.

Next, the compound of the present invention (4-1, 4-7, 4-9, 4-10, 4-11, 5-2, 6-1, 6-3, 6-8 or 6-13) was added to the first layer and color photographic paper samples were prepared in the same manner as the preparation of the Sample No. 101. These samples were incubated under the same condition as above and then exposed and developed also in the same manner as above, and the same results were obtained.

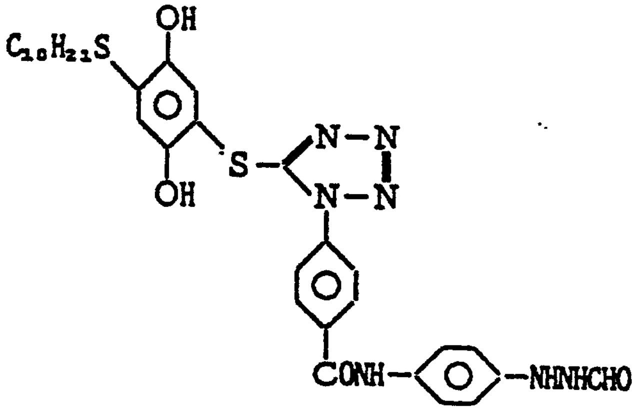
The compound of the present invention (4-1, 4-3, 5-4, 6-2, 6-8 or 6-9) wad added to the fifth layer and color photographic paper samples were prepared also in the same manner as above. The same results were also obtained.

From the above results, it is evident that not only the maximum image density increases but also the storage stability was improved in direct positive color photographic materials by the addition of the compounds of the present invention.

Comparative compound (A′): (described in JP-A-59-170840)



Comparative Compound (B): (described in JP-A-60-107029)



EXAMPLE 2

Color photographic paper samples were prepared in the same manner as in Example 1, except that 3.7 x 10^{-6} mol/mol(Ag) of Nucleating Agent (N-I-16) and 3.0 x 10^{-4} mol/mol(Ag) of Nucleating Agent (A-14) were added to the first, third and fifth layers and that the compound of the present invention was added in an amount of 1.0 x 10^{-4} mol/mol(Ag) as indicated in Tables 3 and 4 below. The thus prepared color photographic paper samples were incubated and then exposed in the same manner as in Example 1, and the thus exposed samples were processed in accordance with process (B) described below. For the processing of the samples, and automatic developing machine having a 5 liter developer tank, a 3 liter bleach-fixing tank and 3 liter rinsing tank was used. Sample No. 201 was first processed in an amount of 20 m^2, and then the remaining samples shown in table 3 or 4 were processed. The color density in the image formed in each sample was measured.

Process (B)	Time	Temperature	Amount of Replenisher
Color Development	90 sec	38°C	290 ml/m^2
Bleach-fixation	45 sec	35°C	290 ml/m^2
Rinsing (1)	30 sec	35°C	
Rinsing (2)	30 sec	35°C	
Rinsing (3)	30 sec	35°C	320 ml/m^2

The replenishment system for the rinsing step was a countercurrent replenishment system in which a replenisher was added to the last rinsing bath (3), and the overflow solution from the rinsing bath (3) was introduced into the previous rinsing bath (2), and the overflow solution from the rinsing bath (2) was also introduced in order into the previous rinsing bath (1). In the process, the amount of the solution as brought into the processing bath from the previous bath together with the photographic paper sample being processed was 35 ml/m^2, and the volume of the replenisher was 9.1 times.

The processing solutions used in process (B) were as follows:

Color Developer:

	Solution	Replenisher
Diethylenetriamine-pentaacetic Acid	0.5 g	0.5 g
1-Hydroxyethylidene-1,1-diphosphonic Acid	0.5 g	0.5 g
Diethylene Glycol	8.0 g	13.0 g
Benzyl Alcohol	12.0 g	18.5 g
Sodium Bromide	0.7 g	-
Sodium Chloride	0.5 g	-
Sodium Sulfite	2.0 g	2.5 g
N,N-diethylhydroxylamine	3.5 g	4.5 g
Triethylenediamine(1,4-diazabicyclo[2,2,2]octane)	3.5 g	4.5 g
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline	5.5 g	8.0 g
Potassium Carbonate	30.0 g	30.0 g
Brightening Agent (Stilbene type)	1.0 g	1.3 g
Pure Water to Make	1000 ml	1000 ml
pH	10.50	10.90
(pH was adjusted by potassium hydroxide or hydrochloric acid.)		

Bleach-fixing Solution:

	Solution (same as Replenisher)
Ammonium Thiosulfate	100 g
Sodium Hydrogen Sulfite	21.0 g
Ethylenediamine-tetraacetic Acid Iron(III) Ammonium Dihydrate	50.0 g
Ethylenediamine-tetraacetic Acid Disodium Dihydrate	5.0 g
Pure Water to Make	1000 ml
pH	6.3
(pH was adjusted by aqueous ammonia or hydrochloric acid.)	

Rinsing Water:

Pure water was used, and the mother liquid and replenisher were the same.

The pure water used was a city water purified by ion-exchange treatment, in which the concentration of all cations except hydrogen ions and that of all anions except hydroxyl ions were 1 ppm or less.

Table 3

No.	Compound Added	Layer Added	Color Measured	Incubation				Note
				No		Yes		
				Dmax	Dmin	Dmax	Dmin	
201	No	-	Cyan	2.1	0.10	1.5	0.15	Control
202	"	-	Magenta	2.0	0.10	1.6	0.15	"
203	"	-	Yellow	2.0	0.10	1.6	0.15	"
204	Comparative compound (A)	1st Layer	Cyan	2.2	0.10	1.7	0.13	Comparison
205	"	3rd Layer	Magenta	2.0	0.10	1.7	0.13	"
206	Comparative compound (B)	1st Layer	Cyan	2.3	0.10	2.1	0.11	"
207	"	5th Layer	Yellow	2.2	0.10	2.1	0.11	"
208	1-1	1st Layer	Cyan	2.5	0.10	2.4	0.11	The Invention
209	1-3	"	"	2.5	0.10	2.5	0.11	"
210	1-18	"	"	2.4	0.10	2.3	0.10	"
211	2-1	"	"	2.3	0.10	2.3	0.11	"
212	3-1	"	"	2.3	0.10	2.2	0.11	"
213	3-9	"	"	2.5	0.10	2.4	0.10	"

Table 3 (continued)

No.	Compound Added	Layer Added	Color Measured	Incubation				Note
				No		Yes		
				Dmax	Dmin	Dmax	Dmin	
214	1-1	3rd Layer	Magenta	2.4	0.10	2.3	0.10	The Invention
215	1-4	"	"	2.4	0.10	2.4	0.10	"
216	1-6	"	"	2.4	0.10	2.3	0.10	"
217	2-2	"	"	2.3	0.10	2.2	0.11	"
218	3-8	"	"	2.5	0.10	2.5	0.10	"
219	3-10	"	"	2.5	0.10	2.4	0.11	"
220	1-1	5th Layer	Yellow	2.4	0.10	2.3	0.10	"
221	1-2	"	Magenta	2.5	0.10	2.4	0.10	"
222	1-9	"	"	2.4	0.10	2.3	0.11	"
223	3-2	"	"	2.4	0.10	2.2	0.11	"
224	3-10	"	"	2.5	0.10	2.4	0.10	"

From the results shown in Table 3, it is clear that Samples Nos. 208 to 224 of the present invention were superior to Control Samples Nos. 201 to 203, since the Dmax value was higher both before and after incubation, and that the Dmin value hardly increased after incubation. In addition, the Samples of the present invention were also superior to the Comparative Samples Nos. 204 to 207 (each containing the Comparative Compound (A) or (B) shown in Example 1), since the Dmax value was higher both before and after incubation.

Table 4

No.	Compound Added	Layer Added	Color Measured	Incubation				Note
				No		Yes		
				Dmax	Dmin	Dmax	Dmin	
201	No	-	Cyan	2.1	0.10	1.5	0.15	Control
202	"	-	Magenta	2.0	0.10	1.6	0.15	"
203	"	-	Yellow	2.0	0.10	1.6	0.15	"
204′	Comparative compound (A′)	1st Layer	Cyan	2.2	0.10	2.1	0.10	Comparison
205′	"	3rd Layer	Magenta	2.2	0.10	2.1	0.11	"
206	Comparative compound (B)	1st Layer	Cyan	2.3	0.10	2.1	0.11	"
207	"	5th Layer	Yellow	2.2	0.10	2.1	0.11	"
225	4-1	1st Layer	Cyan	2.4	0.10	2.3	0.10	The Invention
226	4-3	"	"	2.4	0.10	2.4	0.11	"
227	4-8	"	"	2.3	0.10	2.3	0.11	"
228	5-1	"	"	2.3	0.10	2.2	0.10	"
229	6-1	"	"	2.4	0.10	2.3	0.10	"
230	6-9	"	"	2.5	0.10	2.4	0.10	"

Table 4 (continued)

No.	Compound Added	Layer Added	Color Measured	Incubation				· Note
				No		Yes		
				Dmax	Dmin	Dmax	Dmin	
231	4 -1	3rd Layer	Magenta	2.4	0.10	2.3	0.11	The Invention
232	4 -4	"	"	2.4	0.10	2.3	0.11	"
233	4 -7	"	"	2.4	0.10	2.3	0.10	"
234	5 -2	"	"	2.3	0.10	2.2	0.11	"
235	6 -8	"	"	2.5	0.10	2.4	0.10	"
236	6 -10	"	"	2.4	0.10	2.4	0.11	"
237	4 -1	5th Layer	Yellow	2.4	0.10	2.3	0.11	"
238	4 -2	"	"	2.4	0.10	2.3	0.11	"
239	4 -10	"	"	2.3	0.10	2.2	0.11	"
240	6 -2	"	"	2.4	0.10	2.2	0.11	"
241	6 -10	"	"	2.4	0.10	2.3	0.11	"

From the result in Table 4, it is seen that Samples Nos. 225 to 241 of the present invention were superior to Control Samples Nos. 201 to 203, since the Dmax value was higher both before and after incubation and the Dmin value hardly increased after incubation. In addition, the Samples of the present invention were also superior to the Comparative Samples Nos. 204′, 205′, 206 and 207 (each containing the Comparative Compound (A′) or (B) shown in Example 1), since the Dmax value was higher both before and after incubation.

EXAMPLE 3

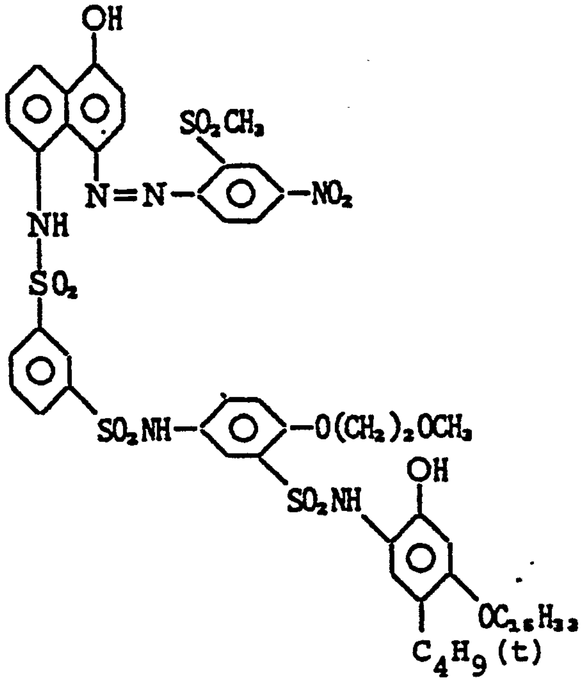
Example 1 and Example 2 were repeated except that the Emulsion (B) was used in place of the Emulsion (A), and the same results were obtained.

EXAMPLE 4

The following layers (1) to (11) were coated on a black support in order to prepare a light-sensitive sheet.

(1) Layer containing the following Cyan DRR Compound (0.36 mmol/m^2), tricyclohexyl phosphate (0.09 g/m^2), 2,5-di(t-pentadecyl)hydroquinone (0.01 g/m^2) and gelatin (0.44 g/m^2).

Cyan DRR Compound:



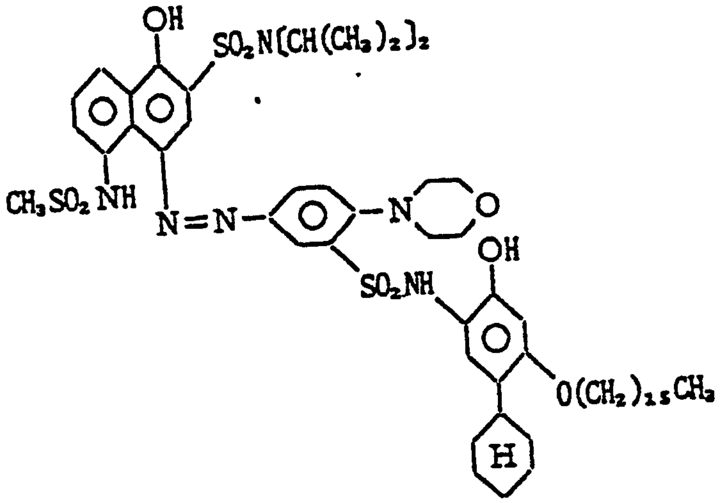
(2) Layer containing a red-sensitive internal latent image-type direct reversal silver bromide emulsion (Emulsion A, containing Red-sensitive Sensitizing Dye mentioned in Example 1) (0.5 g/m^2 as Ag), gelatin (0.78 g/m^2), Nucleating Agent N-II-11 (27 µg/m^2) and sodium pentadecylhydroquinone sulfonate (0.06 g/m^2).

(3) Layer containing 2,5-d-(tert-pentadecyl)hydroquinone (0.71 g/m^2), vinylpyrrolidone/vinyl acetate copolymer (7/3, by molar ratio) (0.24 g./m^2) and gelatin (0.4 g/m^2).

(4) Layer containing gelatin (0.3 g/m^2).

(5) Layer containing the following Magenta DRR Compound (0.49 g/m^2), tricyclohexyl phosphate (0.08 g/m^2), 2,5-di(tert-pentadecyl)hydroquinone (0.01 g/m^2) and gelatin (0.5 g/m^2).

Magenta DRR Compound:



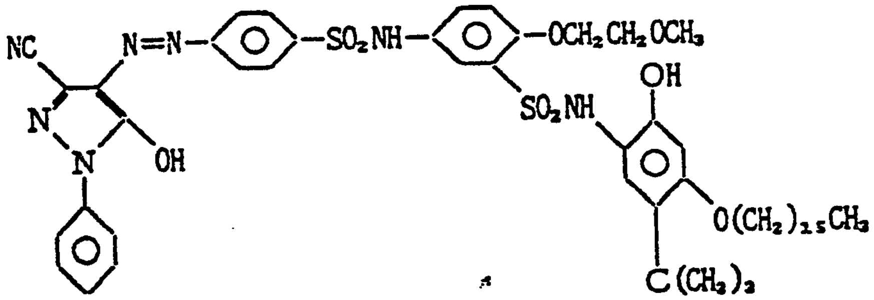
(6) Layer containing a green-sensitive internal latent image-type direct reversal silver bromide emulsion (Emulsion A containing Green-sensitive Sensitizing Dye described in Example 1) (0.34 g/m^2 as silver), gelatin (0.66 g/m^2), the same nucleating agent as Layer (2) (12.9 µg/m^2) and sodium pentadecylhydroquinonesulfonate (0.04 g/m^2).

(7) Layer containing 2,5-d-(tert-pentadecyl)hydroquinone (0.71 g/m^2), vinylpyrrolidone/vinyl acetate copolymer (7/3, by molar ratio) (0.24 g/m^2) and gelatin (0.4 g/m^2).

(8) Layer containing gelatin (0.25 g/m^2).

(9) Layer containing the following Yellow DRR Compound (0.48 g/m^2), tricyclohexyl phosphate (0.03 g/m^2), 2,5-di(tert-pentadecyl)hydroquinone (0.004 g/m^2) and gelatin (0.43 g/m^2).

Yellow DRR Compound:



(10) Layer containing a blue-sensitive internal latent image-type direct reversal silver bromide emulsion (Containing Emulsion A and Blue-sensitive Sensitizing Dye mentioned in Example 1) (0.84 g/m^2 as Ag), gelatin (0.9 g/m^2), the same nucleating agent as in Layer (2) (29 mg/m^2) and sodium pentadecylhydroquinonesulfonate (0.05 g/m^2).

(11) Layer containing gelatin (1.0 g/m^2).

A processing composition having the following components (0.8 g) was put in a container capable of being broken under pressure.

Processing Composition:

Benzyl Alcohol	0.20 ml
1-(P-tolyl)-4-hydroxymethyl-4-methyl-3-pyrazolidinone	0.3 g
Methylhydroquinone	0.012 g
5-Methylbenzotriazole	0.6 g
Sodium Sulfite	0.18 g
Hydroxymethyl Cellulose	4 g
Potassium Hydroxide (28% aqueous solution)	22.4 ml
Water	67 ml

The following layers (12) to (16) were coated in order on the surface of a white support the apposite surface of which had been coated with a carbon black layer and a titanium white layer in order, to prepare a color image-receiving sheet.

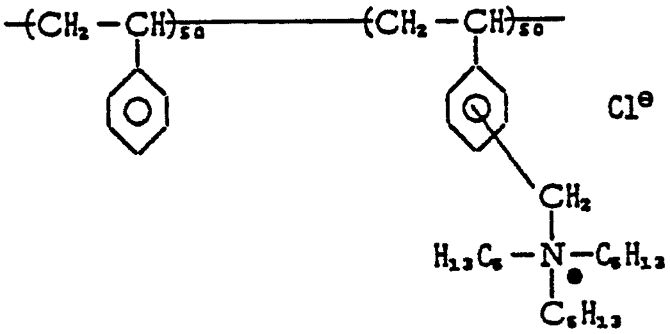
(12) Layer containing acrylic acid/butyl acrylate copolymer (80/20, by weight) (22 g/m^2) and 1,4-bis-(2,3-epoxypropoxy)-butane (0.44 g/m^2).

(13) Layer containing acetyl cellulose (capable of providing 39.4 g of acetyl group by hydrolysis of 100 g of acetyl cellulose) (3.8 g/m^2), styrene/maleic anhydride copolymer (60/40, by weight; molecular weight, about 50,000) (0.2 g/m^2) and 5-(β-cyanoethylthio)-1-phenyltetrazole (0.115 g/m^2).

(14) Layer containing vinylidene chloride/methyl acrylate/acrylic acid copolymer latex (85/12/3, by weight) (3.5 g/m^2) and polymethyl methacrylate latex (grain size, 1 to 3 µm) (0.05 g/m^2).

(15) Mordant layer containing the following mordanting agent (3.0 g/m^2) and gelatin (3.0 g/m^2).

Mordant Agent:



(16) Layer containing phthalated gelatin (1 g/m^2).

The above-mentioned light-sensitive sheet was called Sample No. 401 (control). Other samples were prepared in the same manner as the preparation of the Sample No. 401 (control). Other samples were prepared in the same manner as the preparation of the Sample No. 401, except that the Comparative Compound (B) (described in Example 1) or the compound of the present invention was added to the layer (2) in an amount of 1 x 10^{-5} mol/mol(Ag) as indicated in Table 5 below.

The thus-prepared samples were incubated in an atomosphere of 40°C and 80 %RH for 3 days and then exposed. The thus-exposed sample was attached to the above-mentioned color image-receiving sheet in face-to-face relation and the above-mentioned processing composition was spread therebetween in a thickness of 60 µm by the use of a pressing means. Thus a transferred color image was obtained.

The maximum cyan image density was measured in every sample, and the results obtained were shown in Table 5 below.

Table 5

No.	Compound Added	Dmax		Note
		Before Incubation	After Incubation	
401	No	2.2	1.5	Control
402	Comparative Compound (B)	2.4	2.2	Comparison
403	3-1	2.6	2.4	The Invention
404	3-2	2.6	2.4	"
405	3-7	2.8	2.7	"
406	3-8	2.8	2.7	"
407	3-9	2.8	2.6	"
408	3-10	2.8	2.7	"
409	3-11	2.6	2.5	"
410	3-14	2.7	2.5	"

The compound was added to the 6th layer or 10th layer and the same experiment was repeated using the respective samples. The same results were also obtained.

Still other samples were also prepared in the same manner as the preparation of the control Sample No. 401, except that the Comparative Compound (B) (described in Example 1) or the compound of the present invention was added to the layer (2) in an amount of 1 x 10^{-5} mol/mol(Ag) as indicated in Table 6 below.

The thus-prepared samples were incubated in an atmosphere of 40°C and 80 %RH for 3 days and then exposed. The thus-exposed sample was attached to the above-mentioned color image-receiving sheet and the above-mentioned processing composition was spread therebetween in a thickness of 60 µm by the use of a pressing means. Thus a transparent color image was obtained.

The maximum cyan image density was measured in every sample, and the results obtained were shown in Table 6 below.

Table 6

No.	Compound Added	Dmax		Note
		Before Incubation	After Incubation	
401	No	2.2	1.5	Control
402	Comparative Compound (B)	2.4	2.2	Comparison
411	6 -1	2.5	2.4	The Invention
412	6 -2	2.5	2.4	"
413	6 -5	2.6	2.5	"
414	6 -8	2.6	2.5	"
415	6 -9	2.6	2.5	"
416	6-10	2.6	2.5	"
417	6-13	2.5	2.4	"
418	6-14	2.5	2.3	"

In addition, the compound was added to the 6th layer or 10th layer and the same experiment was repeated using the respective samples. The same results were also obtained.

EXAMPLE 5

Core/shell type emulsions (I), (II) and (III) were prepared each in accordance with the method mentioned below.

Emulsion (I):

1000 ml of aqueous 13% potassium bromide solution and 1000 ml of aqueous 17% silver nitrate solution were a simultaneously added to an aqueous 3% gelatin solution with vigorously, stirring, over a period of about 20 minutes, while the pAg value of the reaction system was controlled to 7.90 at 40°C. Thus a cubic monodisperse silver bromide emulsion having a mean grain size of 0.08 µm was obtained. To the emulsion were added sodium thiosulfate and chloroauric acid (tetra-hydrate) each in an amount of 580 mg per mol of Ag, and the whole was heated at 75°C for 80 minutes for chemical sensitization. The thus-obtained silver bromide grains, as cores, were further grown under the same precipitation conditions as in the first step to finally obtain a core/shell type monodisperse cubic silver bromide emulsion having a mean grain size of 0.18 µm. After washing with water and desalting, sodium thiosulfate and chloroauric acid (tetra-hydrate) were added to the emulsion each in an amount of 6.2 mg per mol of Ag and heated for 60 minutes at 65°C for chemical sensitization. Thus Emulsion (I) was obtained.

Emulsion (II):

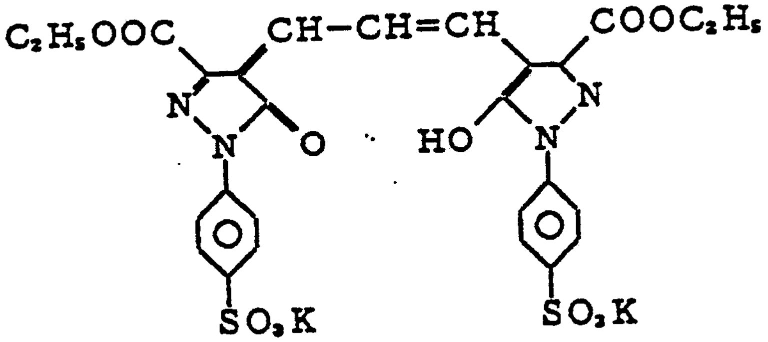
1000 ml of aqueous 13% potassium bromide solution and 1000 ml of aqueous 17% silver nitrate solution were a simultaneously added to an aqueous 3% gelatin solution with vigorously, stirring, over a period of about 40 minutes, while the pAg value of the reaction system was controlled to be 9.70 at 45°C. Thus an octahedral silver bromide emulsion having a mean grain size of 0.2 µm was obtained. To the emulsion were added sodium thiosulfate and chloroauric acid (tetra-hydrate) each in an amount of 5 mg per mol of Ag, and the whole was heated at 75°C for 80 minutes for chemical sensitization. The thus-obtained silver bromide grains, as cores, were grown for a further 40 minutes under the same precipitation conditions as in the first step to finally obtain a core/shell silver bromide emulsion having a mean grain size of 0.35 µm. To the emulsion were added sodium thiosulfate and chloroauric acid (tetra-hydrate) each in an amount of 4.5 mg per mol of Ag, and the whole heated for 60 minutes at 65°C for chemical sensitization. Thus an internal latent image-type silver halide emulsion (Emulsion II) was obtained.

Emulsion (III):

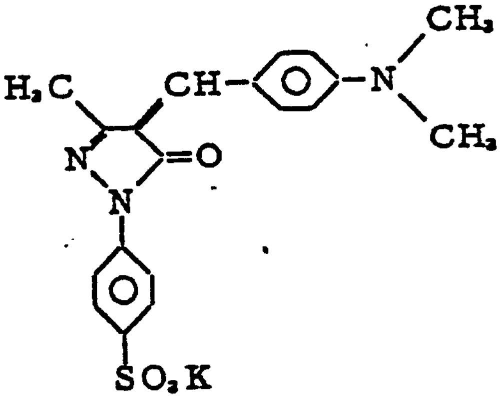
An aqueous potassium bromide solution and an aqueous silver nitrate solution were simultaneously added to an aqueous gelatin solution with vigorous stirring, over a period of about 40 minutes, while the pAg value of the reaction system was controlled to be 8.60 at 75°C. Thus an octahedral monodisperse silver bromide emulsion having a mean grain size of 0.4 µm was obtained. To the emulsion were added sodium thiosulfate and chloroauric acid (tetra-hydrate) each in an amount of 4 mg per mol of Ag, and the whole was heated at 75°C for 80 minutes for chemical sensitization. The thus-obtained silver bromide grains, as cores, were grown for a further 40 minutes under the same precipitation conditions as in the first step to finally obtain an octahedral monodisperse core/shell silver bromide emulsion having a mean grain size of 0.6 µm. After washing with water and desalting, sodium thiosulfate was added to the emulsion in an amount of 0.9 mg per mol of Ag, and the heated for 60 minutes at 65°C for chemical sensitization. Thus an internal latent image-type silver halide emulsion (Emulsion III) was obtained.

A 100 µm thick polyethylene terephthalate support having a subbing layer was prepared. an anti-halation layer (lower layer) composed of Anti-halation Dyes (A), (B) and (C) (65 mg/m^2, 80 mg/m^2 and 40 mg/m^2, respectively) and gelatin (5 g/m^2), and a protective layer (upper layer) composed of barium strontium sulfate (mean grain size 1.0 µm) (0.1 g/m^2) and polymethyl methacrylate (mean grain size 1.3 µm) (0.07 g/m^2), as a matting agent, and Coating Aid (D) (30 mg/m^2), Antistatic Agent (E) (1 mg/m^2), Hardening Agent (F) (100 mg/m^2) and gelatin (1 g/m^2) were coated on the support to form a two-layered backing layer thereon.

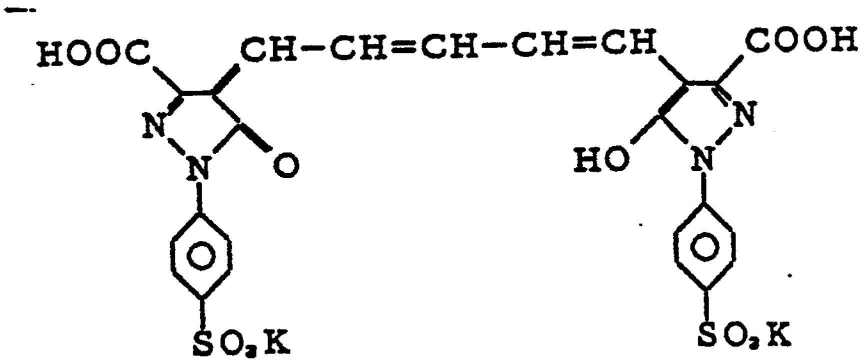
Dye (A):


C₂H₅OOC
CH−CH=CH
COOC₂H₅
N
N
O
HO
N
N
SO₃K
SO₃K

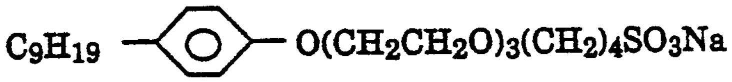
Dye (B):


H₃C
CH
N
CH₃
CH₃
N
N
=O
SO₃K

Dye (C):



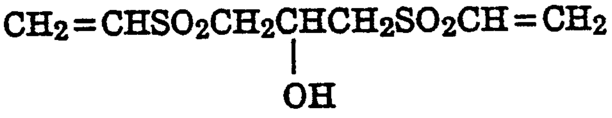
Coating Aid (D):



Antistatic Agent (E):

$$\underset{\displaystyle C_3H_7}{C_8F_{17}SO_3NCH_2COOK}$$

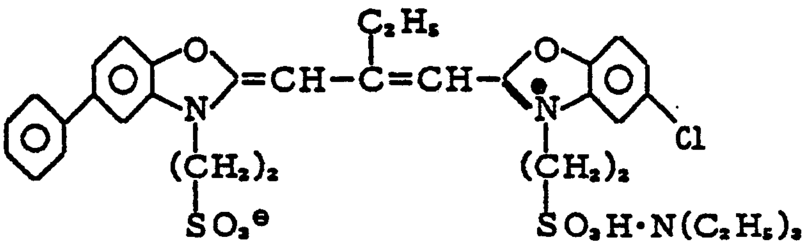
Hardening Agent (F):



$$\underset{\displaystyle OH}{CH_2{=}CHSO_2CH_2CHCH_2SO_2CH{=}CH_2}$$

Sinsitizing Dye (G) was added to Core/shell Emulsions (I), (II) and (III), in an amount of 150 mg, 200 mg and 180 mg, respectively, per mol of Ag, and Nucleating Agent (N-II-1) was also added thereto each in an amount of 1.0 x 10^{-3} mol per mol of Ag. Further, sodium dodecylbenzene sulfonate as a coating aid and additionally a tackifier were added thereto so as to balance the surface tension with the viscosity. Thus coating compositions for first to third layers were prepared.

Sensitizing Dye (G):



Antistatic Agent (E), 0.015 g/m² of sodium dodecylbenzenesulfonate (coating aid) and a tackifier were added to gelatin to prepare a coating composition for 4th layer (protective layer).

The thus-prepared coating compositions for the 1st to 4th layers were coated in order of the above-mentioned support on the surface opposite to that coated with the backing layer. The amount of the first layer coated was 1 g/m² (as Ag); that of the second layer was 0.8 g/m² (as Ag); and that of the third layer was 1.5 g/m² (as Ag). The amount of gelatin in the first layer coated was 1.3 g/m²; that in the second layer was 1.3 g/m²; that in the third layer was 2.4 g/m²; and that in the fourth layer was 1.7 g/m². Thus a direct positive photographic material sample (Sample No. 501) was prepared.

Other samples were prepared in the same manner as in the preparation of Sample No. 501, except that the Comparative Compound (B) (described in Example 1) or the compound of the present invention was added to the emulsion layer in an amount of 5×10^{-5} mol per mol of Ag, as indicated in Table 7 below.

The thus-prepared samples were wedgewise exposed with a 1 kw tungsten lamp (color temperature, 2854° K) for one second through a step-wedge and then developed with an automatic developing machine (FMCP-4800 Type Camera Processor, by Fuji Photo Film Co.) using Developer (D) containing the following Replenisher (A) (one liter) and Starter (B) (20 ml), at 36° C for one minute. After development, the samples were stopped, fixed, rinsed in water and then dried in a conventional manner. The maximum density (Dmax) and the minimum density (Dmin) of the image formed in each sample were measured, and the results obtained were shown in Table 7 below.

Replenisher (A):

Sodium Sulfite	100 g
Potassium Carbonate	20 g
1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	3g
Hydroquinone	45 g
5-Methylbenzotriazole	40 mg
Water to make	1 liter
Potassium Hydroxide to make	pH of 11.8

Starter (B):

Sodium Bromide	175 g
Glacial Acetic Acid	63 ml
Water to make	1 liter

As is evident from Table 7 below, the compounds of the present invention were advantageous since they were effective in an increase of Dmax without an increase of Dmin as compared with the control Sample No. 501 and Comparative Sample No. 502.

Table 7

No.	Compound Added	Dmax	Dmin	Note
501	No	2.81	0.15	Control
502	Comparative Compound (B)	2.92	0.17	Comparison
503	3-1	3.09	0.17	The Invention
504	3-4	3.11	0.17	"
505	3-6	3.15	0.17	"
506	3-7	3.14	0.17	"
507	3-8	3.17	0.16	"
508	3-9	3.18	0.15	"
509	3-10	3.17	0.15	"
510	3-14	3.15	0.17	"

Still other samples were prepared in the same manner as in the preparation of Sample No. 501, except that the Comparative Compound (B) (described in Example 1) or the compound of the present invention was added to the emulsion layer in an amount of 1 x 10^{-5} mol per mol of Ag, as indicated in Table 8 mentioned below.

The thus-prepared samples were wedgewise exposed with a 1 kw tungsten lamp (color temperature, 2854° K) for one second through a step-wedge and then developed with an automatic developing machine (FMCP-4800 Type Camera Processor, by Fuji Photo Film Co.) using Developer (D) containing the following Replenisher (A) (one liter) and Starter (B) (20 ml), at 36° C for one minute. After development, the samples were stopped, fixed, rinsed in water and then dried in a conventional manner. The maximum density (Dmax) and the minimum density (Dmin) of the image formed in each sample were measured, and the results obtained were shown in Table 8 below.

Replenisher (A):

Sodium Sulfite	100 g
Potassium Carbonate	20 g
1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	3 g
Hydroquinone	45 g
5-Methylbenzotriazole	40 mg
Water to make	1 liter
Potassium Hydroxide to make	pH of 11.8

Starter (B):

Sodium Bromide	175 g
Glacial Acetic Acid	63 ml
Water to make	1 liter

As is clear from Table 8 below, the compounds of the present invention were advantageous since they were effective for elevating the Dmax value without elevating the Dmin value, as compared with the control Sample No. 501 and Comparative Sample No. 502′.

Table 8

No.	Compound Added	Dmax	Dmin	Note
501	No	2.81	0.15	Control
502	Comparative Compound (B)	2.92	0.17	Comparison
511	6 -1	3.01	0.17	The Invention
512	6 -3	3.02	0.17	"
513	6 -5	3.25	0.18	"
514	6 -7	3.12	0.17	"
515	6 -8	3.22	0.15	"
516	6 -9	3.25	0.15	"
517	6 -10	3.21	0.15	"
518	6 -11	3.10	0.17	"

EXAMPLE 6

210 ml of aqueous 10% silver nitrate solution and 148 ml of aqueous 10% potassium bromide solution were simultaneously added to an aqueous gelatin solution (pH 5.5, 75°C) containing 20 mg/liter of thioether(1,8-dihydroxy-3,6-dithiaoctane) at a constant rate with constant stirring, while the silver electrode potential was kept -30mV such that regular octahedral grains could grow. 1/8 mol of silver nitrate was added over a period of 5 minutes. Thus an octahedral AgBr monodisperse emulsion having a mean grain size of about 0.14 µm was obtained. Sodium thiosulfate and chloroauric acid (tetra-hydrate) were added to the emulsion each in an amount of 20 mg per mol of the silver halide and it was well stirred at pH of 7.5 at 75°C for 80 minutes for chemical sensitization. Thus a core emulsion was prepared. Afterward 500 ml of aqueous 29.4% silver nitrate solution (containing 7/8 mol of silver nitrate) and 500 ml of aqueous 20% potassium bromide were added to the emulsion also simultaneously at the same temperature 40°C over a period of 40 minutes with constant stirring, whereupon the silver electrode potential was kept -30mV such that regular octahedral grains could grow, so that the cores were coated with shells. Thus a monodisperse octahedral core/shell type emulsion having a mean grain size of about 0.3 µm was obtained. The thus-prepared emulsion was washed with water and desalted in a conventional manner, and then melted under heat. After the pH value of the emulsion was adjusted to 6.5, sodium thiosulfate and chloroauric acid (tetra-hydrate) were added thereto each in an amount of 5 mg per mol of the silver halide and ripened for 60 minutes at 75°C whereby the shell surface was chemically sensitized. Thus an internal latent image- type monodisperse octahedral core/shell type emulsion (Emulsion X) was finally obtained. The grain size distribution of the emulsion was measured from the electro-microscopic photograph thereof, and as a result, the mean grain size was 0.30 µm and the variation coefficient (mean grain size x 100/standard deviation) was 10%.

A panchromatic sensitizing dye(3,3′-diethyl-9-methyl-thiacarbocyanine) was added to the emulsion in an amount of 5 mg per mol of the silver halide, and then Nucleating Agent (N-II-13) (1.0 x 10^{-5}mol per mol of silver halide) and Nucleation Accelerator (A-16) (1 x 10^{-3} mol per mol of silver halide) were added thereto. The resulting composition was coated on a polyethylene terephthalate support in an amount of 2.8 g/m^2 as Ag, after which a protective layer containing gelatin and 0.15 g/m^2 of hardening agent was simultaneously coated thereover. Thus a direct positive photographic material sample sensitive to red light (Sample No. 601) was prepared.

Other samples were prepared in the same manner as in the preparation of Sample No. 601, except that the Comparative Compound (B) (described in Example 1) or the compound of the present invention was added to the emulsion layer in an amount of 5 x 10^{-5} mol per mol of Ag, as indicated in Table 9 below.

The thus-prepared samples were wedgewise exposed with a 1 kw tungusten lamp (color temperature, 2854°K) for 0.1 second through a step-wedge. Next, the thus exposed samples were developed with an automatic developing machine (Kodak Proster I Processor) using Kodak Proster Plus processing solution (developer, pH 10.7) at 38°C for 18 seconds and successively rinsed in water, fixed, again rinsed in water and then dried. the process was all performed in the same developing machine. The maximum density (Dmax) and the minimum density (Dmin) of the direct positive image formed in each sample were measured, and the results obtained were shown in Table 9 below.

Table 9

No.	Compound Added	Dmax	Dmin	Note
601	No	2.62	0.06	Control
602	Comparative Compound (B)	2.69	0.07	Comparison
603	3-1	2.81	0.07	The Invention
604	3-4	2.94	0.07	"
605	3-7	2.95	0.07	"
606	3-8	2.92	0.07	"
607	3-10	2.94	0.07	"
608	3-11	2.80	0.07	"
609	3-14	2.87	0.07	"

As is evident from the results shown in Table 9 above, the compounds of the present invention (Sample Nos. 603 to 609) were advantageous since these were effective for elevating the Dmax value without elevating the Dmin value, as compared with the Comparative Sample No. 602.

Still other samples were prepared also in the same manner as in the preparation of Sample No. 601, except that the Comparative Compound (B) (described in Example 1) or the compound of the present invention was added to the emulsion layer in an amount of 1 x 10^{-4} mol per mol of Ag, as indicated in Table 10 mentioned below.

The thus-prepared samples were wedgewise exposed with a 1 kw tungsten lamp (color temperature, 2854° K) for 0.1 second through a step-wedge. Next, the thus exposed samples were developed with an automatic developing machine (Kodak Proster I Processor) using Kodak Proster Plus processing solution (developer, pH 10.7) at 38° C for 18 seconds and successively rinsed in water, fixed, again rinsed in water and then dried. The process was all performed in the same developing machine. The maximum density (Dmax) and the minimum density (Dmin) of the direct positive image formed in each sample were measured, and the results obtained were shown in Table 10 below.

Table 10

No.	Compound Added	Dmax	Dmin	Note
601	No	2.62	0.06	Control
602	Comparative Compound (B)	2.69	0.07	Comparison
610	6 -1	2.71	0.07	The Invention
611	6 -2	2.73	0.07	"
612	6 -7	2.72	0.07	"
613	6 -8	2.85	0.07	"
614	6 -10	2.83	0.07	"
615	6 -14	2.71	0.07	"
616	6 -15	2.73	0.07	"

As is clear from the results shown in Table 10 above, the compounds of the present invention (Sample Nos. 610 to 616) were advantageous since these were effective for elevating the Dmax value without elevating the Dmin value, as compared with the Comparative Sample No. 602.

EXAMPLE 7

The layers each having the composition mentioned below were coated in order on a cellulose triacetate film support having a subbing layer to prepare a multi-layer color photographic material sample (Sample No. 701).

Preparation of Sample No. 701:

The amounts of the respective components are represented in units of g/m², and the amount of the silver halide means the amount of silver therein. the amount of the sensitizing dye is represented in units of mol per mol of the silver halide in the dye-containing layer.

First layer: anti-halation Layer

Black Colloidal Silver	0.18 as Ag
Gelatin	0.40

Second Layer: Interlayer

2,5-Di-t-pentadecylhydroquinone	0.18
EX-1	0.07
EX-3	0.02
EX-11	0.005
U-1	0.08
U-2	0.08
HBS-1	0.10
HBS-2	0.02
Gelatin	1.04

Third Layer: First Red-sensitive Emulsion Layer

Silver Iodobromide Emulsion (silver iodide 6 mol%, mean grain size 0.70 μm)	0.55 as Ag
Sensitizing Dye I	6.9×10^{-5}
Sensitizing Dye II	1.8×10^{-5}
Sensitizing Dye III	3.1×10^{-4}
Sensitizing Dye IV	4.0×10^{-5}
EX-2	0.350
HBS-1	0.005
EX-10	0.042
Gelatin	1.20

Fourth Layer: Second Red-sensitive Emulsion Layer

Silver Iodobromide Emulsion (silver iodide 8 mol%, mean grain size 0.75 μm)	1.20 as Ag
Sensitizing Dye I	5.1×10^{-5}
Sensitizing Dye II	1.4×10^{-5}
Sensitizing Dye III	2.3×10^{-4}
Sensitizing Dye IV	3.0×10^{-5}
EX-2	0.300
EX-3	0.050
EX-10	0.004
HBS-2	0.050
Gelatin	1.30

Fifth Layer: Third Red-sensitive Emulsion Layer

Silver Iodobromide Emulsion (silver iodide 14 mol%, mean grain size 1.00 µm)	1.60 as Ag
Sensitizing Dye I	5.4×10^{-5}
Sensitizing Dye II	1.4×10^{-5}
Sensitizing Dye III	2.4×10^{-4}
Sensitizing Dye IV	3.1×10^{-5}
EX-5	0.150
EX-3	0.055
EX-4	0.060
HBS-1	0.32
Gelatin	1.63

Sixth Layer: Interlayer

HBS-3	0.01
Gelatin	1.06
EX-14	0.02

Seventh Layer: First Green-sensitive Emulsion Layer

Silver Iodobromide Emulsion (silver iodide 6 mol%, mean grain size 0.65 µm)	0.40 as Ag
Sensitizing Dye V	3.0×10^{-5}
Sensitizing Dye VI	1.0×10^{-4}
Sensitizing Dye VII	3.8×10^{-4}
EX-6	0.260
EX-1	0.021
EX-7	0.030
EX-8	0.025
HBS-1	0.100
HBS-4	0.060
Gelatin	0.75

Eighth Layer: Second Green-sensitive Emulsion Layer

Silver Iodobromide Emulsion (silver iodide 9 mol%, mean grain size 0.70 µm)	0.80 as Ag
Sensitizing Dye V	2.1×10^{-5}
Sensitizing Dye VI	7.0×10^{-5}
Sensitizing Dye VII	2.6×10^{-4}
EX-6	0.150
EX-8	0.010
EX-1	0.008
EX-7	0.012
HBS-1	0.60
HBS-4	0.050
Gelatin	0.10

Ninth Layer: Third Green-sensitive Emulsion Layer

Silver Iodobromide Emulsion (silver iodide 12 mol%, mean grain size 1.0 µm)	1.2 as Ag
Sensitizing Dye V	3.5×10^{-5}
Sensitizing Dye VI	8.0×10^{-5}
Sensitizing Dye VII	3.0×10^{-4}
EX-6	0.065
EX-1	0.025
HBS-2	0.55
Gelatin	1.74

Tenth Layer: Yellow Filter Layer

Yellow Collodial Silver	0.05 as Ag
EX-14	0.04
HBS-1	0.02
Gelatin	0.95

Eleventh Layer: First Blue-sensitive Emulsion Layer

Silver Iodobromide Emulsion (silver iodide 6 mol%, mean grain size 0.6 µm)	0.24 as Ag
Sensitizing Dye VIII	3.5×10^{-4}
EX-9	0.85
EX-8	0.12
HBS-1	0.28
Gelatin	1.28

Twelfth Layer: Second Blue-sensitive Emulsion Layer

Silver Iodobromide Emulsion (silver iodide 10 mol%, mean grain size 0.80 µm)	0.45 as Ag
Sensitizing Dye VIII	2.1×10^{-4}
EX-9	0.20
EX-8	0.015
HBS-1	0.03
Gelatin	0.46

Thirteenth Layer: Third Blue-sensitive Emulsion Layer

Silver Iodobromide Emulsion (silver iodide 16 mol%, mean grain size 1.2 µm)	0.77 as Ag
Sensitizing Dye VIII	2.2×10^{-4}
EX-9	0.20
HBS-1	0.07
Gelatin	0.69

Fourteenth Layer: First Protective Layer

Silver Iodobromide Emulsion (silver iodide 1 mol%, mean grain size 0.07 μm)	0.08 as Ag
U-1	0.11
U-2	0.17
HBS-1	0.90
Gelatin	1.00

Fifteenth Layer: Second Protective Layer

Polymethyl Methacrylate Grains (diameter, about 1.5 μm)	0.54
S-1	0.04
S-2	0.04
Gelatin	0.72

In addition to the above-mentioned components, a gelatin-hardening agent (H-1) and 0.015 g/m^2 of a surfactant were added to the respective layers.

Preparation of Samples Nos. 702 to 714:

Samples Nos. 702 to 714 were prepared in the same manner as the preparation of the Sample No. 701, except that the compound (A) or (B) (described in Example 1) was added to the 13th layer in an amount of 1×10^{-4} mol per mol of Ag, as indicated in Table 11 below.

A part of these samples were incubated in a refrigerator at 6 °C and 80 %RH for 7 days and another part thereof were incubated under the condition of 40°C and 80 %RH for 7 days. Then these were sensitometrically exposed with a white light and then color-developed in accordance with the process described below. The density of the thus-processed samples was measured with a blue light. The results obtained were shown in Table 11 below.

The color development was effected in accordance with the following process at 38°C.

Color Development	3 min 15 sec
Bleaching	6 min 30 sec
Rinsing in Water	2 min 10 sec
Fixation	4 min 20 sec
Rinsing in Water	3 min 15 sec
Stabilization	1 min 05 sec

The processing solutions used in the respective steps had the following compositions.

Color Developer:

Diethylenetriamine-pentaacetic Acid	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic Acid	2.0 g
Sodium Sulfite	4.0 g
Potassium Carbonate	30.0 g
Potassium Bromide	1.4 g
Potassium Iodide	1.3 mg
Hydroxylamine Sulfate	2.4 g
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline Sulfate	4.5 g
Water to make	1.0 liter
pH	10.0

Bleaching Solution:

Ethylenediamine-tetraacetic Acid Ferric Ammonium Salt	100.0g
Ethylenedimaine-tetraacetic Acid Disodium Salt	10.0 g
Ammonium Bromide	150.0 g
Ammonium Nitrate	10.0 g
Water to make	1.0 liter

pH 6.0

Fixing Solution:

Ethylenedimaine-tetraacetic Acid Disodium Salt	1.0 g
Sodium Sulfite	4.0 g
Ammonium Thiosulfate Aqueous Solution (70 wt.%)	175.0 ml
Sodium Bisulfite	4.6 g
Water to make	1.0 liter

pH 6.6

Stabilizing Solution:

Formalin (40 wt.%)	2.0 ml
Polyoxyethylene-p-monononylphenylether (mean polymerization degree 10)	0.3 g
Water to make	1.0 liter

Table 11

No.	Compound Added	Samples Incubated under Cool Conditions		Samples Incubated under High Temperature and High Humidity Conditions		Note
		Dmin	Relative Sensitivity*	Dmin	Relative Sensitivity*	
701	No	0.50	100	0.50	98	Control
702	Comparative Compound (A)	0.51	101	0.52	100	Comparison
703	Comparative Compound (B)	0.53	106	0.55	101	"
704	1-1	0.51	115	0.52	113	The Invention
705	1-3	0.51	117	0.52	115	"
706	1-10	0.51	113	0.51	112	"
707	1-17	0.52	115	0.53	114	"
708	2-2	0.53	120	0.54	118	"
709	3-1	0.53	119	0.53	115	"
710	3-7	0.52	121	0.53	118	"
711	3-8	0.52	118	0.53	116	"
712	3-9	0.52	119	0.54	117	"
713	3-11	0.51	117	0.53	115	"
714	3-15	0.52	118	0.54	115	"

(*) Relative Sensitivity: This corresponds tot he reciprocal of an exposure giving a colored density of (fog + 0.2), based on the standardized value (100) of the control Sample No. 701 incubated under cool conditions.

The results in Table 11 demonstrate that the compounds of the present invention (Samples Nos. 704 to 714) were effective for elevating the sensitivity, while the fog level was almost same in both the samples of the present invention and the Comparative Samples (Nos. 702 and 703).

Preparation of Samples Nos. 702′, 703 and 715 to 725:

Samples Nos. 702′, 703 and 715 to 725 were prepared in the same manner as the preparation of the Sample No. 701, except that the compound of the present invention or the Comparative Compound (A′) or (B) (described in Example 1) was added to the 13th layer in an amount of 5 x 10^{-5} mol per mol of Ag, as indicated in Table 12 below.

A part of these samples were incubated in a refrigerator and another part thereof were incubated under the conditions of 40° C and 80 %RH for 7 days. Then these were sensitometrically exposed with a white light and then color-developed in accordance with the same process as mentioned above. The density of the thus processed samples was measured with a blue light. The results obtained were shown in Table 12 below.

Table 12

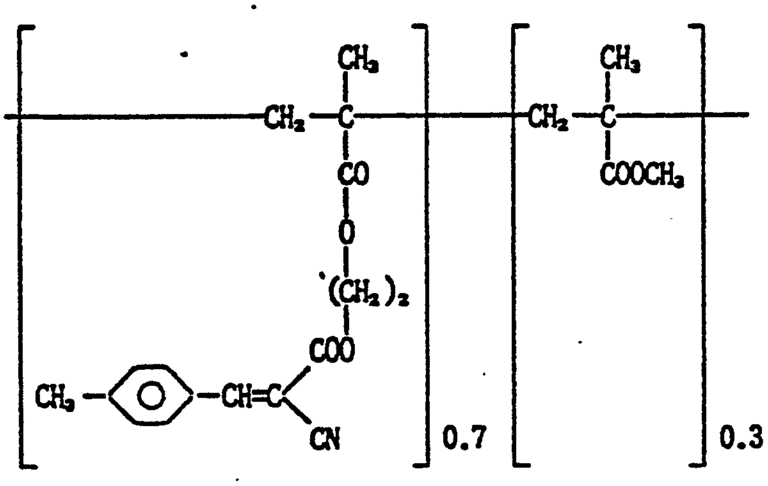
No.	Compound Added	Samples Incubated under Cool Conditions		Samples Incubated under High Temperature and High Humidity Conditions		Note
		Dmin	Relative Sensitivity*	Dmin	Relative Sensitivity*	
701	No	0.50	100	0.50	98	Control
702	Comparative Compound (A')	0.52	105	0.53	102	Comparison
703	Comparative Compound (B)	0.53	106	0.55	101	"
715	4 -1	0.52	115	0.52	114	The Invention
716	4 -3	0.52	116	0.52	115	"
717	4 -6	0.51	113	0.52	112	"
718	4-10	0.52	115	0.53	113	"
719	5 -2	0.52	120	0.54	117	"
720	6 -1	0.53	118	0.55	115	"
721	6 -3	0.53	119	0.55	117	"
722	6 -8	0.52	123	0.53	122	"
723	6 -9	0.52	121	0.53	120	"
724	6-11	0.51	120	0.53	119	"
725	6 -3	0.52	117	0.54	115	"

(*) Relative Sensitivity: This corresponds tot he reciprocal of an exposure giving a colored density of (fog + 0.2), based on the standardized value (100) of the control Sample No. 701 incubated under cool conditions.

The results in Table 12 demonstrate that the compounds of the present invention (Samples Nos. 715 to 725) were effective for elevating the sensitivity, while the fog level was almost same in both the samples of the present invention and the Comparative Samples (Nos. 702 and 703).

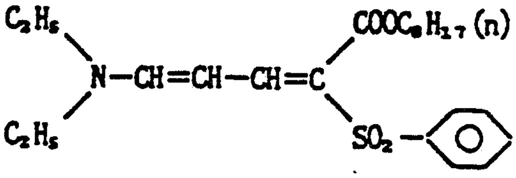
The compounds used in Example 7 had the following structural formulae.

U-1:



(average molecular wieght 50,000)

U-2:



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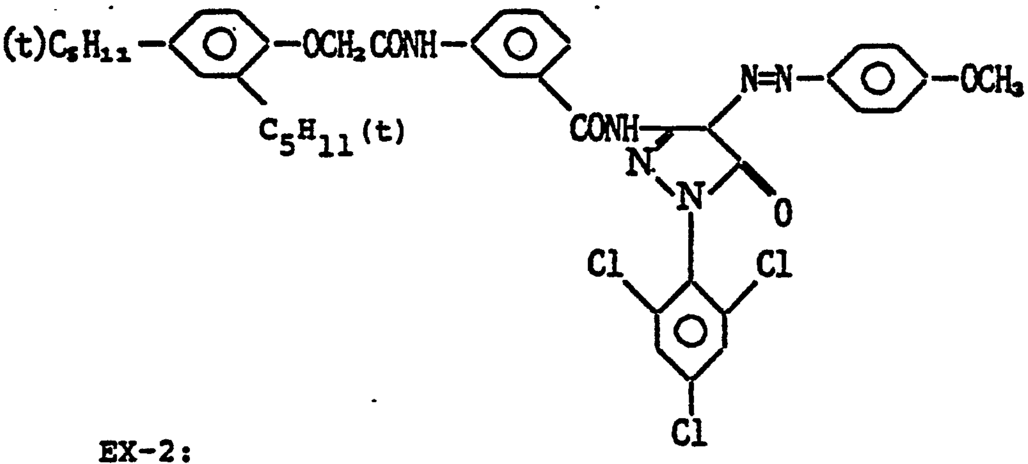

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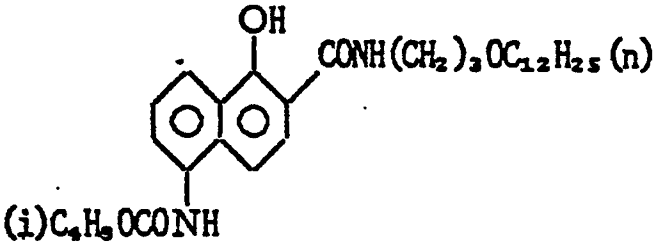

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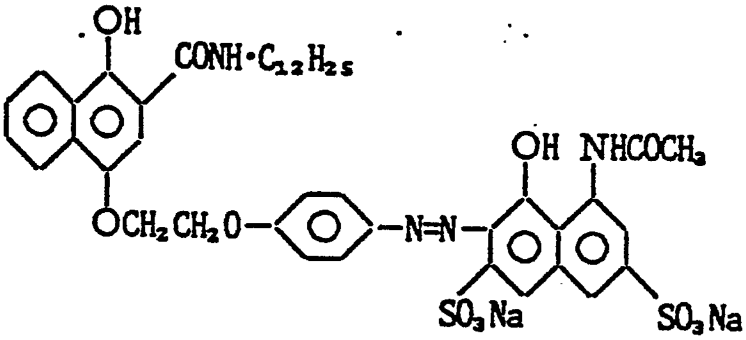

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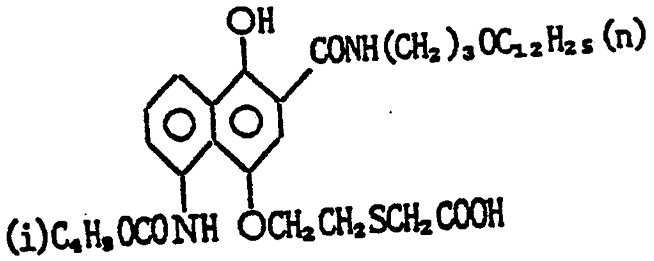

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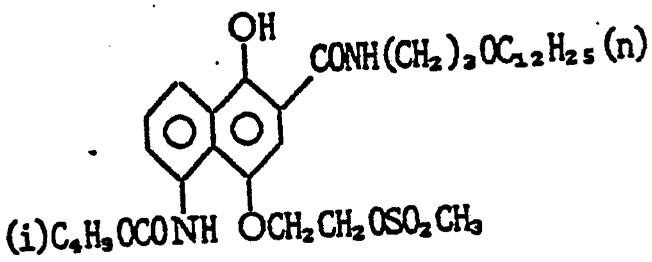
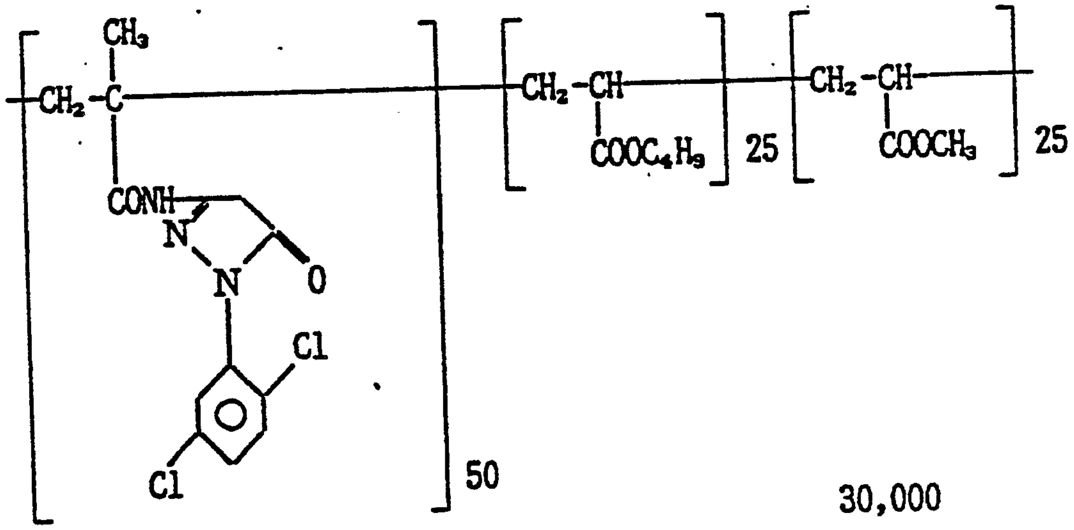
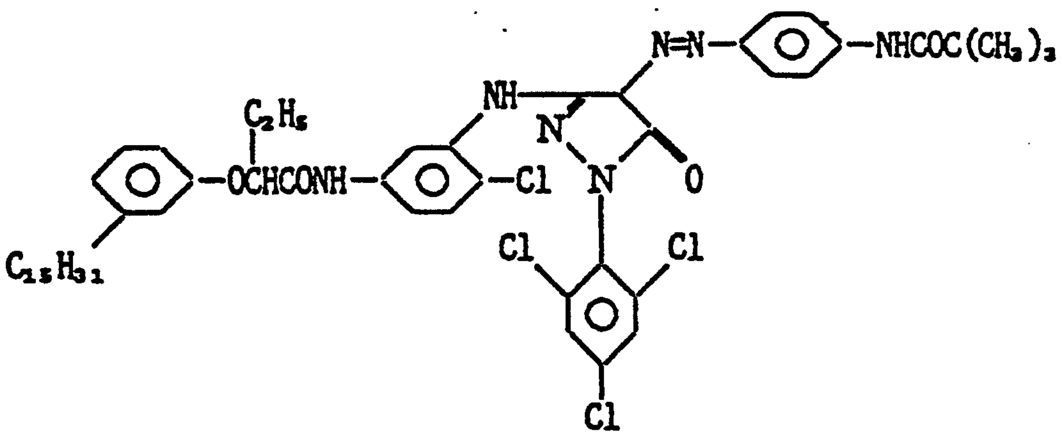


EX-6: (Coupler disclosed in JP-A-58-28745)

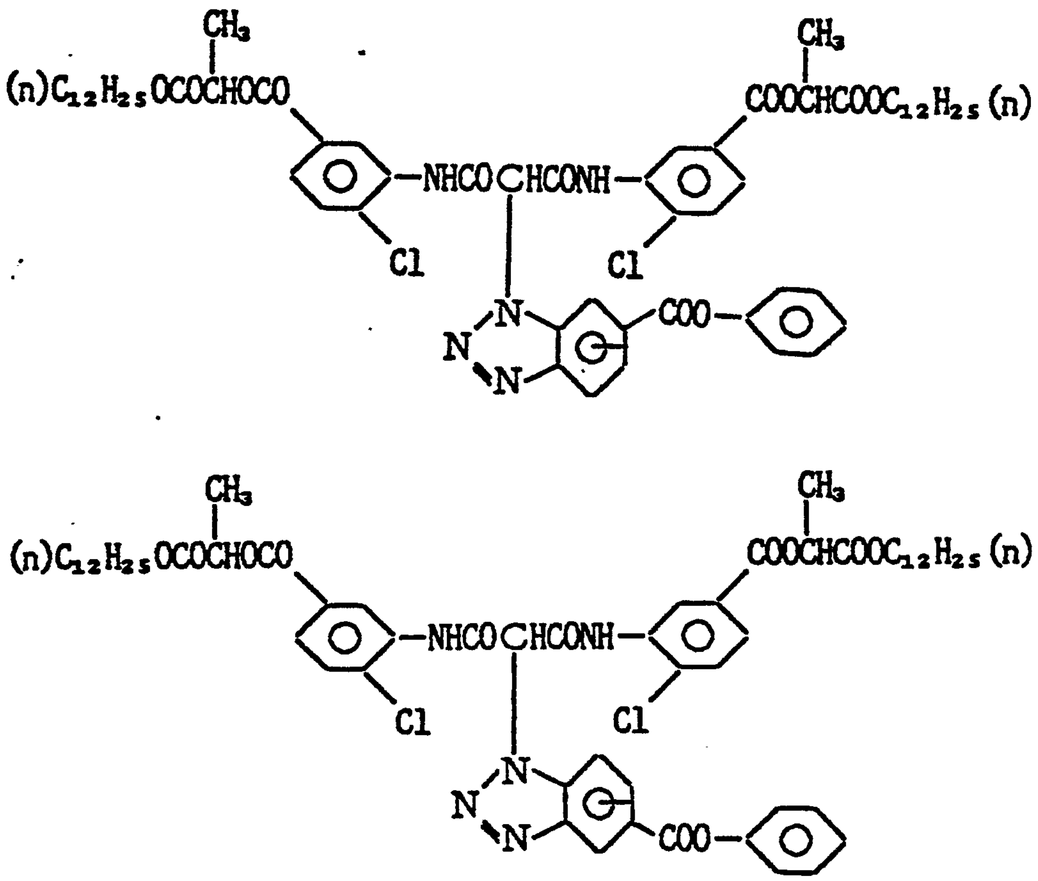


mean molecular weight: 30,000

EX-7:

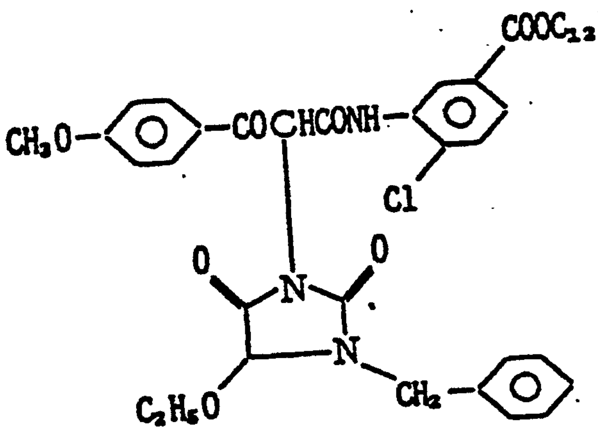


EX-8:

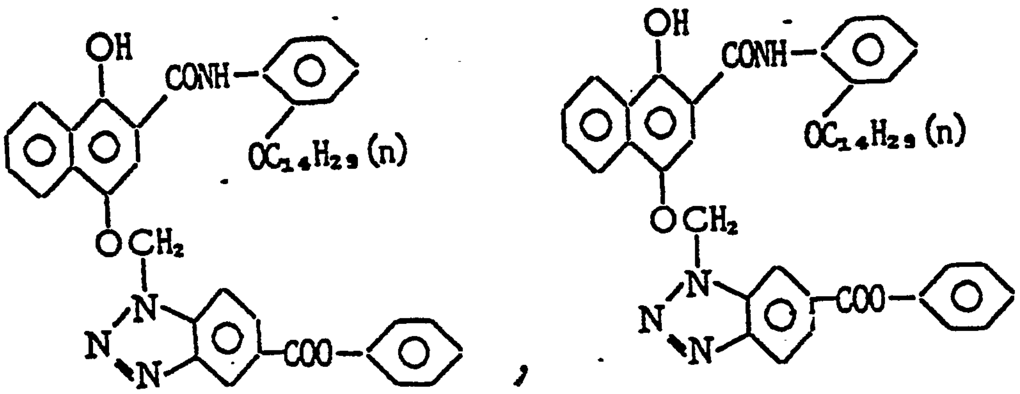


mixture about 1:1 by weight

EX-9:

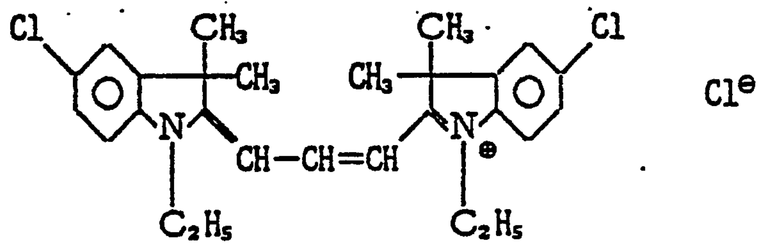


EX-10:



mixture about 1:1 by weight

EX-11:



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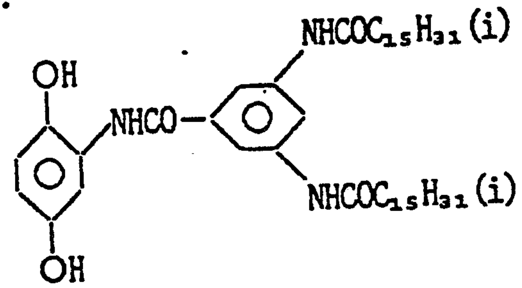
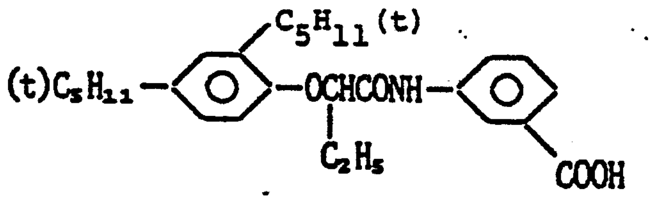
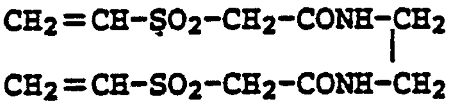


HBS-1: Tricresyl Phosphate
HBS-2: Dibutyl Phthalate
HBS-3: Bis(2-ethylhexyl) Phthalate

HBS-4:

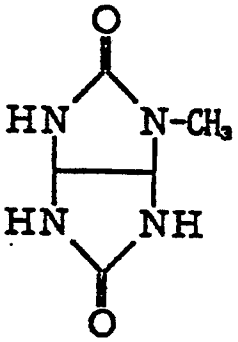


H-1:

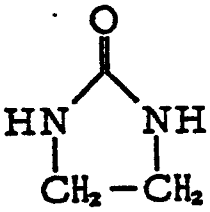


$$\begin{array}{l} CH_2=CH-SO_2-CH_2-CONH-CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2=CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

S-1:



S-2:



Sensitizing Dyes:

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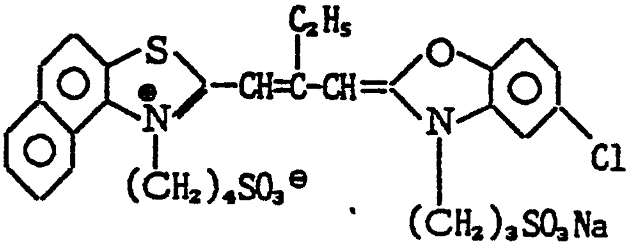

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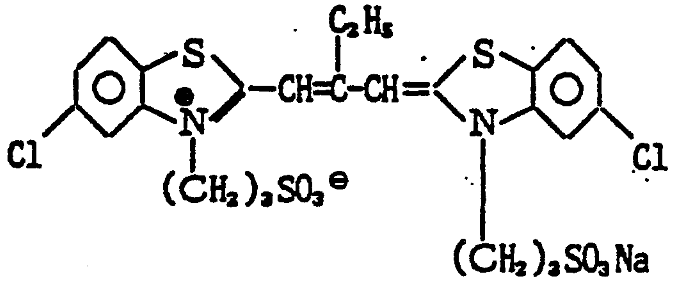

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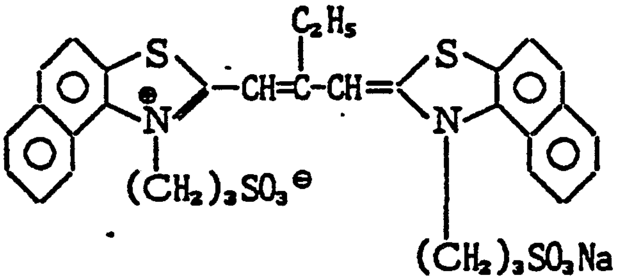

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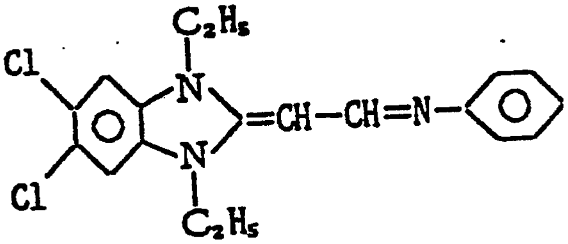

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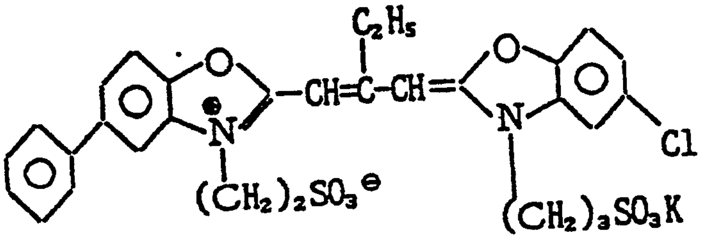

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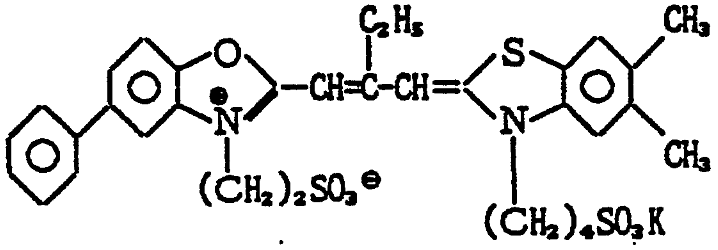
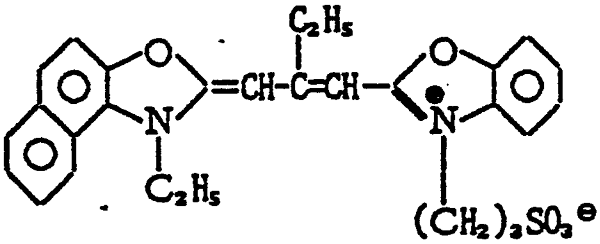


VII:



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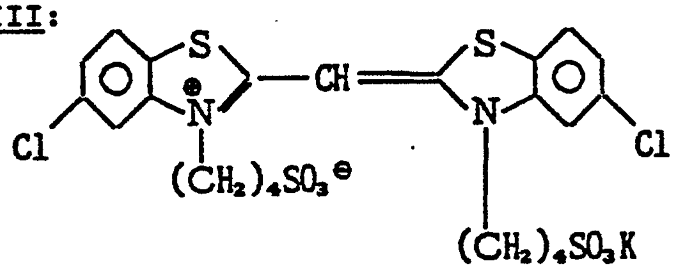
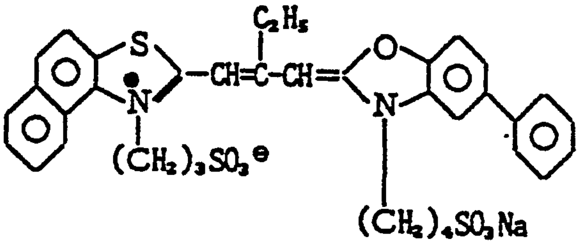


IX:



EXAMPLE 8

Sensitizing Dye E (described below) (9.5 x 10^{-5} mol) and the compound of the present invention (indicated in Tables 13 and 14 below) or the Comparative Compound (B) (discribed in Example 1) (1 x 10^{-3} mol per mol of Ag) were added to a silver bromide emulsion (1 kg) prepared in a conventional manner (having (100) plane), and the resulting emulsion was coated on a triacetate film support and dried to prepare a photographic material sample.

The sample was wedgewise exposed (0.1 sec) with a 3200 lux light through an yellow filter (SC-46, by Fuji Photo Film Co.).

The thus-exposed sample was developed with a developer having the composition mentioned below for 5 minutes at 20° C and then stopped, fixed and rinsed with water by a conventional process. Thus a strip sample having a determined black-and-white image was obtained. The density of the sample was measured with a TCD-type Densitometer (manufactured by Fuji Photo Film Co.) and the yellow filter sensitivity (S_Y) and the fog value were obtained. The relative value obtained on the basis of the standard value (fog + 0.10) of the optical density for determining the sensitivity of each sample was shown for each sample, in Tables 13 and 14 below.

The developer used had the following compositions. Water	500 ml
Metol	2 g
Anhydrous Sodium Sulfite	90 g
Hydroquinone	8 g
Sodium Carbonate (monohydrate)	52.5 g
Potassium Bromide	5 g
Water to make	1 liter

Comparing the relative sensitivity values of the respective samples shown in Tables 13 and 14 below, it is evident that the compounds of the present invention were more effective for elevating the photographic sensitivity than the Comparative Compounds (B).

<u>Sensitizing Dye (E):</u>

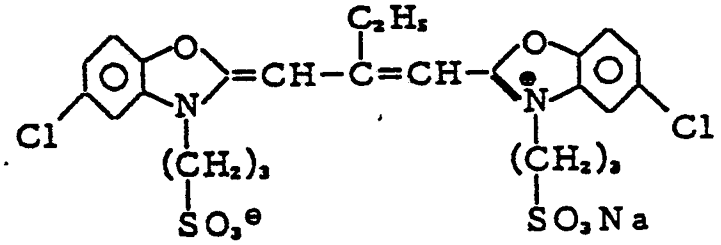


Table 13

No.	Compound Added	Relative Sensitivity	Fog Density	Note
801	No	100	0.04	Control
802	Comparative Compound (B)	118	0.04	Comparison
803	3-2	125	0.04	The Invention
804	3-4	117	0.04	"
805	3-8	121	0.04	"
806	3-10	124	0.04	"
807	3-14	123	0.04	"

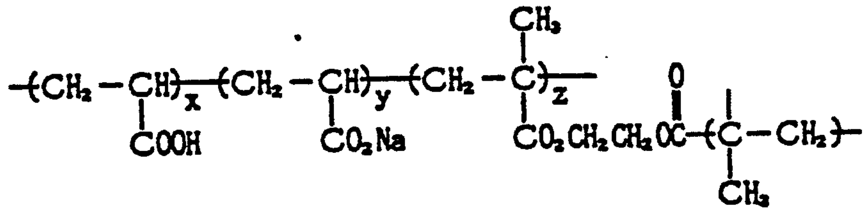
Table 14

No.	Compound Added	Relative Sensitivity	Fog Density	Note
801	No	100	0.04	Control
802	Comparative Compound (B)	118	0.04	Comparison
808	6 -1	125	0.04	The Invention
809	6 -3	127	0.04	"
810	6 -5	135	0.04	"
811	6 -8	128	0.04	"
812	6 -9	129	0.04	"

EXAMPLE 9

Potassium hexachloroiridium (III) (4 x 10^{-7} mol per mol of Ag) was added to an aqueous gelatin solution kept at 50° C, and an aqueous silver nitrate solution and an aqueous solution containing potassium iodide and potassium bromide were simultaneously added thereto over a period of 60 minutes in the presence of ammonia, while the pAg value of the reaction system was kept at 7.8. Thus a cubic monodisperse emulsion having a mean grain size of 0.25 µm and a mean silver iodide content of 1 mol% was obtained. To the silver iodobromide emulsion were added 0.32 g per mol of Ag of sodium 5,5′-dichloro-9-ethyl-3,3′-bis(3-sulfopropyl)oxacarbocyanine, as a sensitizing dye, 0.04 g per mol of Ag of 4-hydroxy-6-methyl-1,3,3a,7-tetra-azaindene, as a stabilizer, a dispersion of polyethylacrylate, 1,3-vinylsulfonyl-2-propanol and the following Nucleating Agent N (5 x 10-3 mol per mol of Ag), and then the following acidic Polymer Latex H (400 mg/m^2) was further added thereto. Then the resulting composition was coated on a polyethylene terephthalate film in an amount of 3.4 gm^2 as Ag, to prepare a photographic material sample (Sample No. 901).

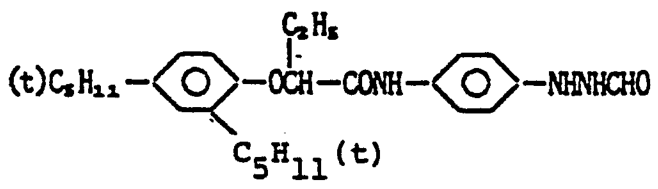
Acidic Polymer Latex H:



$$-(CH_2-\underset{COOH}{CH})_x-(CH_2-\underset{CO_2Na}{CH})_y-(CH_2-\overset{CH_3}{\underset{CO_2CH_2CH_2O\overset{O}{C}-(\underset{CH_3}{C}-CH_2)-}{C}})_z-$$

(particle size 0.08 µ)

N:



Other samples were prepared in the same manner as the preparation of Sample No. 901, except that the compound of the present invention or the Comparative Compound (B) (mentioned in Example 1) was added in an amount of 1 x 10^{-2} mol per mol of Ag, as indicated in Table 15 shown below.

The thus-prepared samples were exposed and developed, and the photographic characteristics of the repective samples were measured. The development was effected with a developer having the composition mentioned below, in an automatic developing machine (FG-660F type, by Fuji Photo Film Co.), at 38° C for 30 seconds.

Developer:

Hydroquinone	45.0 g
N-methyl-p-aminophenol 1/2-Sulfate	0.8 g
Sodium Hydroxide	18.0 g
Potassium Hydroxide	55.0 g
5-Sulfosalicylic Acid	45.0 g
Boric Acid	25.0 g
Potassium Sulfite	110.0 g
Ethylenediamine-tetraacetic Acid Disodium Salt	1.0 g
Potassium Bromide	6.0 g
5-Methylbenzotriazole-n-butyl-diethanolamine	15.0 g
Water to make	1 liter
(pH 11.6)	

In Table 15 below, the relative sensitivity means the reciprocal of the exposure giving a density of 1.5 by development at 38° C for 30 seconds, based on the standardized value (100) of the control Sample No. 901.

The black pepper was evaluated by microscopic observation by way of 5-stage evaluation, in which "5" means the best quality (with no pepper) and "1" means the worst quality (with noticeable pepper). The stages "5" and "4" indicate commercially useful products; the stage "3" indicates rough but marginally useful products; and the stages "2" and "1" indicate unusable products. The intermediate between "4" and "3" was represented by "3.5".

Table 15

No.	Compound Added	Relative Sensitivity	γ	Dmax	Black Pepper	Note
901	No	100	14	3.9	5	Control
902	Comparative Compound (B)	103	15	4.0	4.0	Comparison
903	6-1	104	17	4.2	4.5	The Invention
904	6-2	103	17	4.3	4.5	"
905	6-5	98	18	4.4	4.5	"
906	6-8	102	17	4.3	5.0	"
907	6-9	102	18	4.3	5.0	"
908	6-10	102	18	4.2	5.0	"

The compounds of the present invention (Samples Nos. 903 to 908) were superior to the Comparative Compound (B′) Sample No. 902), since the former were more effective than the latter for elevating Dmax and γ without increasing black pepper.

The present invention provides various advantages which have concretely been demonstrated in the above-mentioned examples and which are summarized as follows.

A direct positive color photographic material having both a high maximum image density and a high discrimination can be obtained.

A direct positive color photographic materials which is excellent in storage stability, especially under conditions of high temperature and high humidity, can be obtained.

A direct positive color photographic material which forms a direct positive image having a sufficiently high color density, even when processed with a highly stable developer with a low pH value, can be obtained.

A negative photographic material having an excellent storage stability and a high sensitivity can be obtained.

A high contract negative photographic material which is sufficiently hard and has high maximum density with almost no black pepper can be obtained.

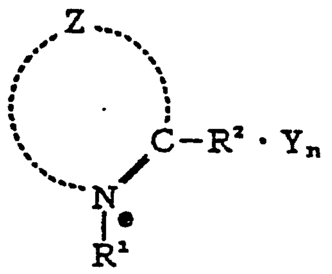
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver halide photographic material comprising a support having thereon at least one light-sensitive sliver halide emulsion layer, at least one layer thereof containing at least one compound capable of releasing a foggant represented by formula (M-1) or (M-2) by at least one of a coupling reaction and a redox reaction with the oxidation product of a developing agent under alkaline conditions during development:

(M-1) $A-(L)_\ell-Q'$

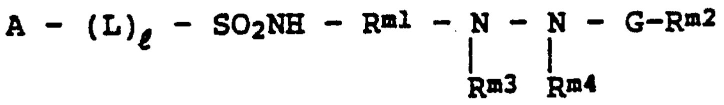
in which A represents a group to accelarate adsorbing a silver halide;
L represents a divalent linking group;
ℓ is 0 or 1;
Q' represents a group derived from a quaternary salt nucleating agent represented by formula Q, by removing any hydrogen redical therefrom:



(Q)

wherein Z represents a substituted or unsubstituted non-metallic atomic group necessary for forming a 5-membered or 6-membered hetero-ring;
R^1 represents a substituted or unsubstituted aliphatic group;
R^2 represents hydrogen, a substituted or unsubstituted aliphatic group or a substituted or unsubstituted aromatic group, and R^2 may be linked to Z to form a ring;
provided that at least one of R^1, R^2 and Z contains an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or R^1 and R^2 are linked to form a 6-membered dihydropyridinium ring;
Y represents a counter ion required for charge balance;
n is 0 or 1; and

(M-2)



$$A-(L)_\ell-SO_2NH-R^{m1}-\underset{\displaystyle R^{m3}}{\underset{|}{N}}-\underset{\displaystyle R^{m4}}{\underset{|}{N}}-G-R^{m2}$$

wherein R^{m1} represents a divalent aromatic group; R^{m2} represents hydrogen, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, an aryloxy group or an amino group;
G represents a carbonyl group, a sulfonyl group, a sulfoxy group, a phosphoryl group or an iminomethylene group $NH=C<$;
one of R^{m3} and R^{m4} represents hydrogen and the other represents hydrogen, an alkylsulfonyl group, an arylsulfonyl group or an acyl group;
A represents a group accelerating the adsorbing to a silver halide;
L represents a divalent linking group; and
ℓ is 0 or 1.

2. The silver halide photographic material as claimed in claim 1 in which said compound capable of releasing a foggant is selected from compounds represented by formulae (1) to (3):

[1] Cp-(TIME)$_m$-M$'$
[2] BALL-Cp-(TIME)$_m$-M$'$
[3] RED-(TIME)$_m$-M$'$

wherein Cp represents a coupler capable of reacting with the oxidation product of an aromatic primary amine developing agent by a coupling reaction to release -(TIME)$_m$-M$'$ in formula (1) and BALL in formula (2);

BALL represents a non-diffusible group;

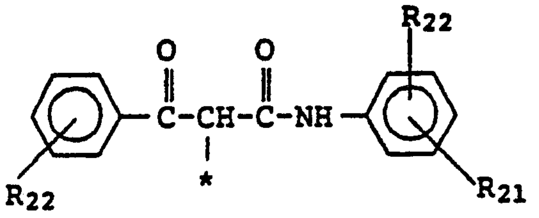
RED represents a group capable of reacting with the oxidation product of a developing agent by a redox reaction to release -(TIME)$_m$-M$'$;

TIME represents a timing group capable of releasing M$'$ after being released from Cp or RED;

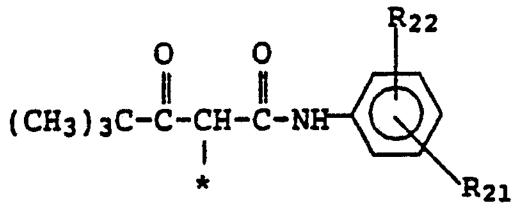
m is 0 or 1;

M$'$ represents a group derived from the compound of formula (M-1) or (M-2) linked to TIME, Cp or RED via A.

3. The silver halide photographic material as claimed in claim 2, wherein Cp is a yellow coupler represented by formulae (Ia) or IIa):



[Ia]



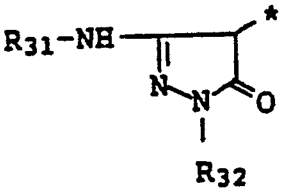
[IIa]

wherein * indicates the position at which the group -(TIME)$_m$-M$'$ is bonded in formulae (1) and (3), and the position at which -BALL is bonded in formula (2);

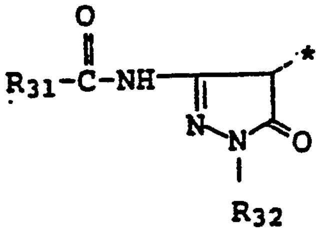
R$_{21}$ represents a non-diffusible group containing from 8 to 32 Carbon atoms;

R$_2$ represents hydrogen, or at least one substituent selected from a halogen atom, a lower alkyl group, a lower alkoxy group and a non-diffusible group of from 8 to 22 carbon atoms, and plural R$_{22}$ groups may be the same or different.

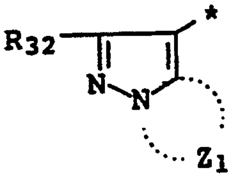
4. The silver halide photographic material as claimed in claim 2, wherein Cp is a magenta coupler represented by formulae (IIIa), (IVa) or (Va):



[IIIa]



[IVa]



[Va]

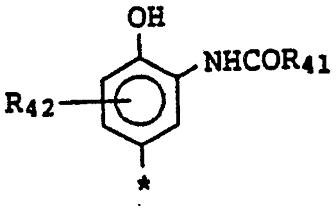
wherein * indicates the position at which the group $-(\mathrm{TIME})_m-\mathrm{M}'$ is bonded in formulae (1) and (3), and the position at which -BALL is bonded in formula (2);

R_{31} represents a non-diffusible group containing from 8 to 32 carbon atoms;

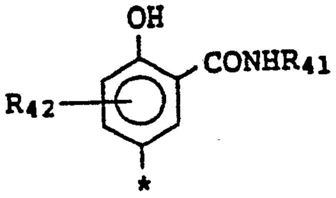
R_{32} represents at least one substituent selected from a halogen atom, a lower alkyl group, a lower alkoxy group, a phenyl group and a substituted phenyl group;

Z_1 represents a substituted or unsubstituted non-metallic atomic group necessary for forming a 5-membered azole ring containing from 2 to 4 nitrogen atoms, or a condensed ring thereof.

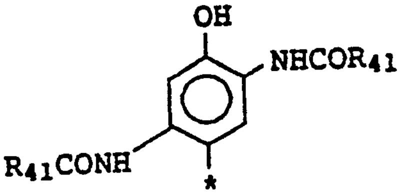
5. The silver halide photographic material as claimed in claim 2, wherein Cp is a cyan coupler represented by formulae (VIa), (VIIa), (VIIIa) or (IXa):



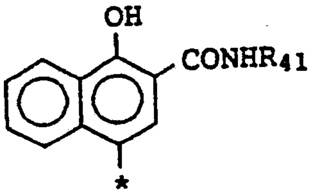
[VIa]



[VIIa]



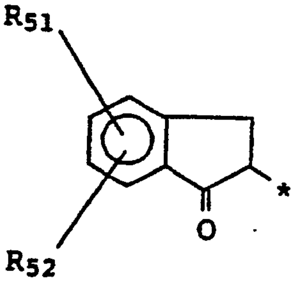
[VIIIa]



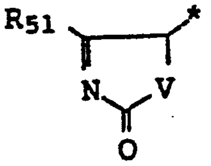
[IXa]

wherein * indicates the position at which the group $-(\mathrm{TIME})_m-M'$ is bonded in formulae (1) and (3), and the position at which -BALL is bonded in formula (2);
R_{41} represents a non-diffusible group containing from 8 to 32 carbon atoms;
R_{42} represents at least one substituent selected from a halogen atom, a lower alkyl group and a lower alkoxy group and
plural R_{42} groups may be the same or different.

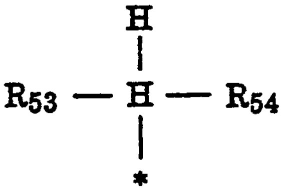
6. The silver halide photographic material as claimed in claim 2, wherein Cp is a colorless coupler represented by formulae (Xa), (XIa) or (XIIa):



[Xa]



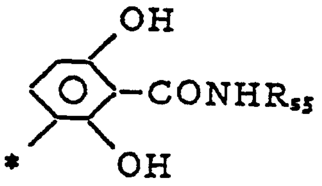
[XIa]



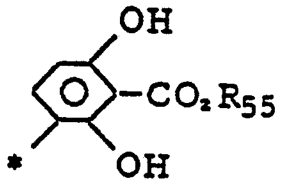
[XIIa]

wherein * indicates the position at which the group -(TIME)$_m$-M$'$ is bonded in formulae (1) and (3), and the position at which -BALL is bonded in formula (2);
R_{51} represents a non-diffusible group containing from 8 to 32 carbon atoms;
R_{52} represents hydrogen, a halogen, a lower alkyl group or a lower alkoxy group;
V represents oxygen, sulfur or nitrogen; and
R_{53} and R_{54} which may be the same or different, represents an alkoxycarbonyl group, an aminocarbonyl group, an acyl group or a sulfonic acid or sulfinic acid derivative of each said group; a cyano group; an ammonium group; or a nitrogen-containing heterocyclic group linked to C via a nitrogen thereof, and R_{53} and R_{54} may be linked to form a 5-membered or 6-membered ring.

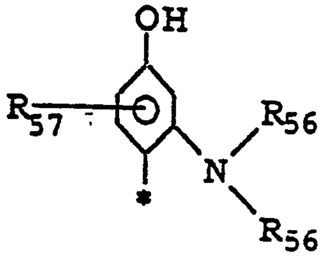
7. The silver halide photographic material as claimed in claim 2, wherein Cp is a black-coloring coupler represented by formulae (XIIIa), (XIVa) or (XVa):



[XIIIa]



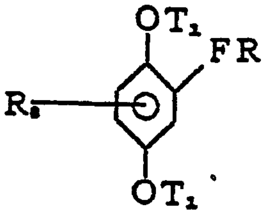
[XIVa]

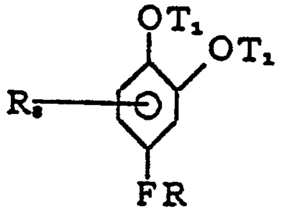


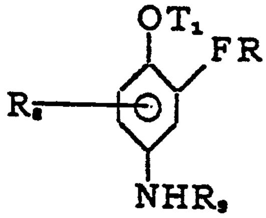
[XVa]

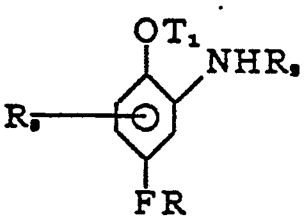
wherein * indicates the position at which the group -(TIME)$_m$-M′ is bonded in formulae (1) and (3), and the position at which -BALL is bonded in formula (2);
R_{55} represents an alkyl group having from 3 to 20 carbon atoms, an unsubstituted phonyl group or a phenyl group substituted with at least one hydroxyl group, halogen atom, amino group, alkyl group containing from 1 to 20 carbon atoms, or alkoxy group;
R_{56} represents hydrogen, a halogen, an alkyl group containing from 1 to 20 carbon atoms, an alkenyl group containing from 1 to 20 carbon atoms, or an aryl group containing from 6 to 20 carbon atoms; and
R_{57} represents a halogen, an alkyl group containing from 1 to 20 carbon atoms, an alkoxy group containing from 1 to 20 carbon atoms or a monovalent organic group; and plural R_{57} groups may be the same or different.

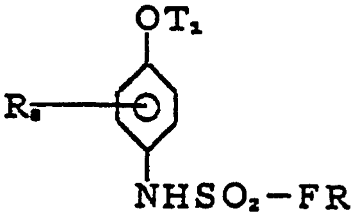
8. The silver halide photographic material as claimed in claim 2, wherein said compound represented by formula (3) is selected from compounds represented by formulae (XVIa) to (XXIa):

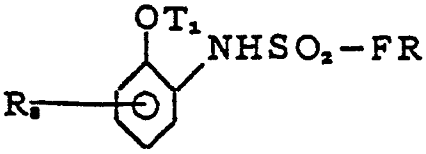

[XVIa]


[XVIIa]


[XVIIIa]


[XIXa]

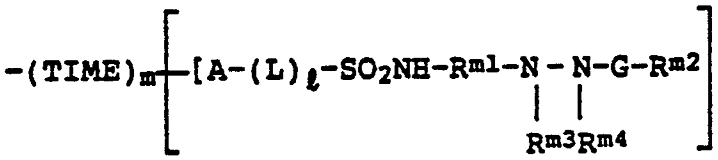

[XXa]


[XXIa]

wherein FR represents said group -(TIME)$_m$-M$'$; and R_8 represents at least one substituent selected from hydrogen, a halogen, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a cyano group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, a carboxyl group, a sulfo group, a sulfonyl group, an acyl group, a carbonamido group, a sulfonamido group, a hydroxyl group, an acyloxy group or a heterocyclic group, and plural R_8 groups may be the same or different, and may be linked to form a ring.

9. The silver halide photographic material as claimed in claim 8 wherein FR represents a group capable of releasing a compound represented by formulae (M-1) or (M-2) under alkaline conditions and is represented by the following formulae (XXII) or (XXIII)

$$-(\mathrm{TIME})_m-[A-(L)_\ell-Q'] \quad \text{or} \qquad [\mathrm{XXII}]$$



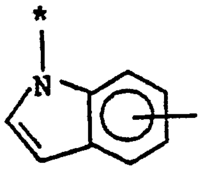
$$-(\mathrm{TIME})_m\left[[A-(L)_\ell-SO_2NH-R^{m1}-\underset{R^{m3}}{\underset{|}{N}}-\underset{R^{m4}}{\underset{|}{N}}-G-R^{m2}\right] \qquad [\mathrm{XXIII}]$$

wherein A, L, Q′, m, ℓ, R^{m1}, R^{m2}, R^{m3}, R^{m4} and G are each as defined in claim 1, and wherein TIME represents a timing group capable of releasing the compound of the formula (M-1) or (M-2) after release of the group FR from RED:

10. The silver halide photographic material as claimed in claim 1, wherein said foggant is represented by formula (M-1).

11. The silver halide photographic material as claimed in claim 1, wherein said foggant is represented by formula (M-2).

12. The silver halide photographic material as claimed in claim 2, wherein A is selected from compounds represented by the following formulae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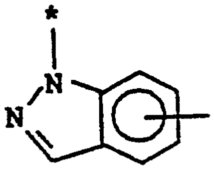
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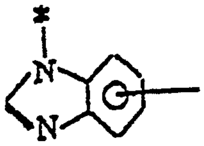
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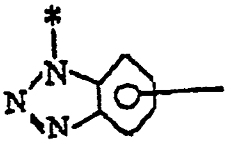
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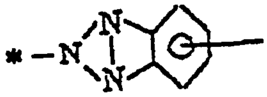
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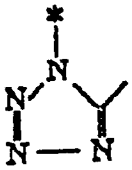
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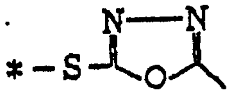
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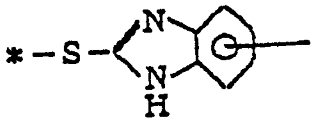
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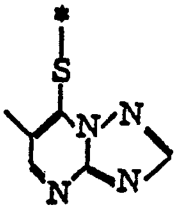


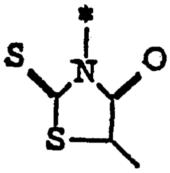
,

$$*-NH\overset{\overset{S}{\|}}{C}NH-$$

,

$$-NH\overset{\overset{S}{\|}}{C}S-*$$

,



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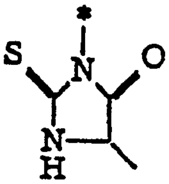
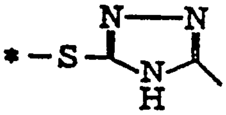


,

$$-CH_2\overset{\overset{S}{\|}}{C}NH-*$$

,



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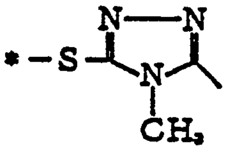
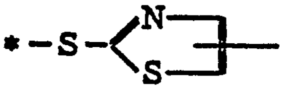
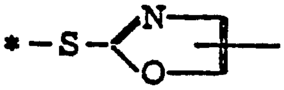

N
N
S
N
CH₃

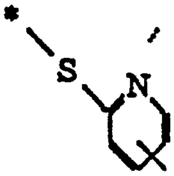
,


S
N
S

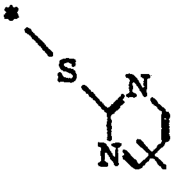
,


S
N
O

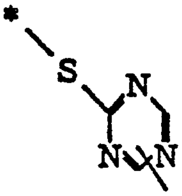
,


S
N

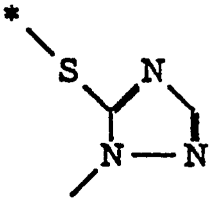
,


S
N
N

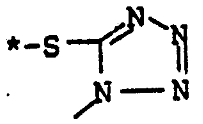
,


S
N
N
N

,


S
N
N
N

,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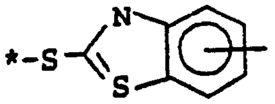
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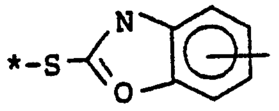
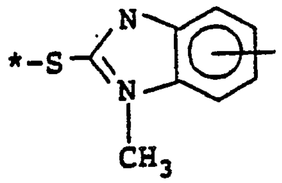

, and 
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wherein * indicates the position at which said group is bonded to -(TIME)$_m$-.

13. The silver halide photographic material as claimed in claim 1, wherein each said L is selected from an alkylene group, an alkenylene group, an arylene group, a divalent heterocyclic group, oxygen, sulfur, an imino group, -COO-, CONH-, -NHCONH-, -NHCOO-, -SO$_2$NH-, -CO-, -SO$_2$-, -SO-, -NHSO$_2$NH- and a combination thereof.

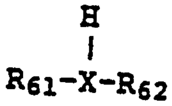
14. The silver halide photographic material as claimed in claim 10, wherein said heterocyclic ring formed by Z is selected from quinolinium, benzothiazolium, benzimidazolium, pyridinium, thiazolinium, thiazolium, napththothiazolium, selenazolium, benzoselenazolium, imidazolium, tetrazolium, indolenium, pyrrolinium, acridinium, phenanthridium, isoquinolinium, oxazolium, naphthoxazolium and benzoxazolium, and said substituted group Z is substituted with at least one substituent selected from an alkyl group, an alkenyl group, an aralkyl group, an aryl group, an alkynyl group, a hydroxyl group, an alkoxy group, an aryloxy group, a halogen, an amino group, an alkylthio group, an arylthio group, an acyloxy group, an acylamino group, a sulfonyl group, a sulfonyloxy group, a sulfonylamino group, a carboxyl group, an acyl group, a carbamoyl group, a sulfamoyl group, a sulfo group, a cyano group, a ureido group, a urethane group, a carbonate group, a hydrazine group, a hydrazone group and an imino group.

15. The silver halide photographic material as claimed in claim 10, wherein said hydrazine group present in R^1, R^2 and Z is substituted with an acyl group or a sulfonyl group; said hydrazone group present in R^1, R^2 and Z is substituted with an aliphatic group or an aromatic group; said acyl group present in R^1, R^2 and Z is a formyl group, an aliphatic ketone or an aromatic ketone; and said alkynyl group present in R^1, R^2 and Z contains from 2 to 18 carbon atoms.

16. The silver halide photographic material as claimed in claim 1, wherein said compound capable of releasing said foggant is present in an amount of from 10^{-9} to 10^{-1} mol per mol of silver contained in said layer containing said compound capable of releasing said foggant, or a layer adjacent thereto.

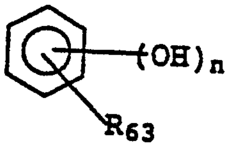
17. The silver halide photographic material as claimed in claim 1 further comprising a formalin scavenger represented by formulae (SI) or (SII):

(SI)



$$R_{61}-\overset{\overset{\displaystyle H}{|}}{X}-R_{62}$$

(SII)



wherein R_{61} and R_{62} which may be the same or different, each represents hydrogen, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an acyl group, an alkoxycarbonyl group, a carbamoyl group or an amino group, and R_{61} and R_{62} may be linked to form a ring; provided that at least one of R_{61} and R_{62} is an acyl group, an alkoxycarbonyl group, a carbamoyl group or an amino group;

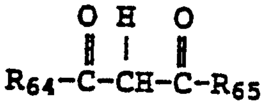
X represents $-\overset{|}{C}H-$ or $-\overset{|}{N}-$;

R_{63} represents hydrogen, an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group, and R_{63} may be linked to the phenyl ring to form a bicyclic compound;

n is an integer of 2 to 5.

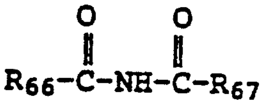
18. The silver halide photographic material as claimed in claim 17, in which the said formalin scavenger is selected from compounds of general formulae (SI-1) to (SI-7), (SII-1) and (SII-2):

[SI-1]



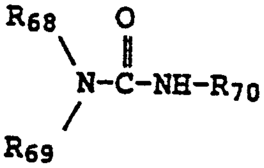
$$R_{64}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}H-\overset{\overset{\displaystyle O}{\|}}{C}-R_{65}$$

[SI-2]



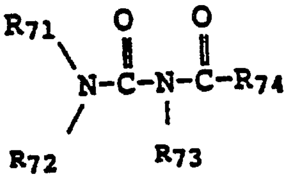
$$R_{66}-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\overset{\overset{\displaystyle O}{\|}}{C}-R_{67}$$

[SI-3]

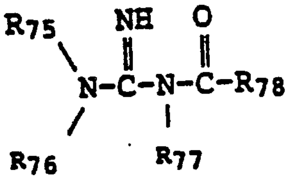


$$(R_{68})(R_{69})N-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R_{70}$$

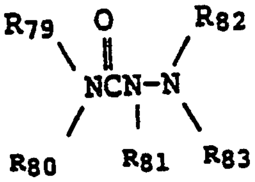
[SI-4]



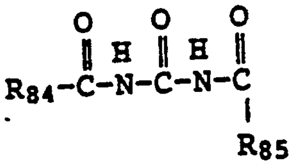
[SI-5]



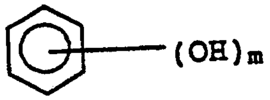
[SI-6]



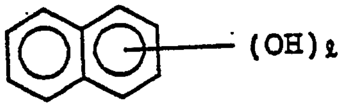
[SI-7]



[SII-1]



[SII-2]



wherein R_{64} to R_{85}, which may be the same or different, each represents hydrogen, an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group, provided that at least one of R_{71}, R_{72}, R_{73} and R_{74} and at least one of R_{79}, R_{80}, R_{81}, R_{82} and R_{83} represents hydrogen; and

R_{64} and R_{65}; R_{66} and R_{67}; and R_{84} and R_{85} each may from a ring; and any two of each of R_{68} to R_{70}; R_{71} to R_{74}; R_{75} to R_{78}; and R_{79} to R_{83} may also form a ring;

m is an integer of from 3 to 6; and

ℓ is an integer of 2 or more.