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(54) **Silver halide color photographic material.**

(57) A silver halide color photographic material containing a compound represented by the following general formula has improved desilvering quality:
(B)•Ag
where (B) is a nitrogenous compound and/or a sulfureous compound, provided that (B) may form a ring.

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SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

BACKGROUND OF THE INVENTION

This invention relates to silver halide color photographic materials for use with cameras that have good desilvering quality.

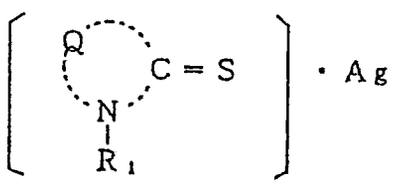
The processing of silver halide color photographic materials (hereinafter sometimes referred to simply as "photographic materials") consists of two basic stages, color development and desilvering, the latter stage consisting of bleaching and fixing steps or a bleach-fixing step. These steps may be combined with additional steps such as rinsing and stabilization.

The demand for increasing the speed of processing of photographic materials is constantly growing and in order to carry out the desilvering step at a higher speed, it has been desired to incorporate a desilvering accelerating technique not only in processing solutions but also in the photographic material per se. Thiols, thiones, dithiones, etc. have been known as bleaching accelerators that are effective in permitting the bleaching step to be carried out with greater rapidity. However, even if these compounds are directly added to photographic materials, their desilvering quality is hardly improved. To the contrary, many defects occur such as decreased sensitivity and lower color densities. Thus, the use of conventional bleaching accelerators is not considered to be an effective technique for increasing the rapidity of desilvering step.

SUMMARY OF THE INVENTION

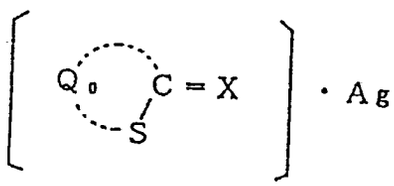
An object, therefore, of the present invention is to provide a silver halide color photographic material that has sufficiently good desilvering quality to shorten the time required for the desilvering step to be completed.

This object of the present invention can be attained by a silver halide color photographic material comprising a support, a light-sensitive silver halide emulsion layer and a non-light-sensitive layer, said material containing at least one of the compounds represented by the following general formulas (I) - (XII) (these compounds are hereinafter sometimes referred to collectively as the "compounds of the present invention"):



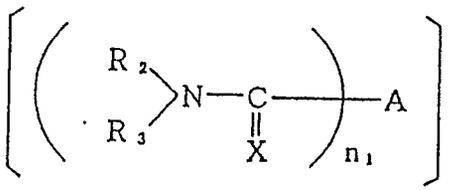
(I)

where Q is the atomic group necessary to form the nitrogenous hetero ring; R_1 is an alkyl group, a cycloalkyl group, an aryl group, a hetero ring or an amino group;



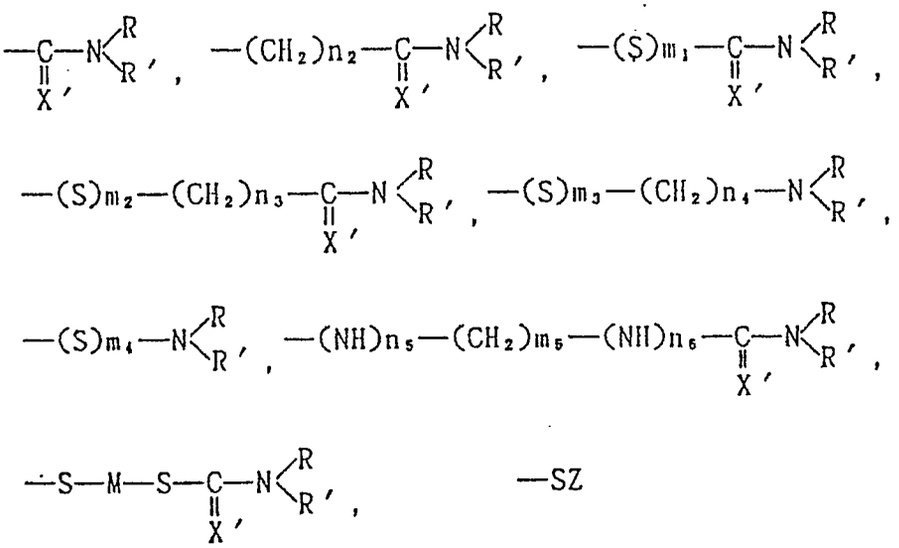
(II)

where Qo is the atomic group necessary to form the sulfureous hetero ring; X is O, S or NR (R is a hydrogen atom or an alkyl group);

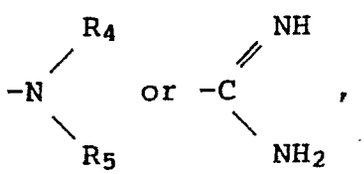


· Ag (III)

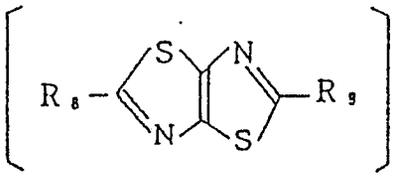
where R_2 and R_3 are each independently a hydrogen atom, an alkyl atom, a hydroxyl group, a carboxyl group, an amino group, an acyl group, an aryl group or an alkenyl group; A is



or an n_1-valent heterocyclic residue; X is =S, =O or =NR″ (where R and R′ respectively have the same meanings as R_2 and R_3; X′ has the same meaning as X; Z is an ammonium group, an amino group, a nitrogenous heterocyclic residue, an alkyl group or -B-Y; M is a divalent group of metallic atoms; R″ is a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic residue or an amino group; n_1 - n_6 and m_1 - m_4 are each an integer of 1 - 6; m_5 is an integer of 0 - 6; B is an alkylene group; Y is

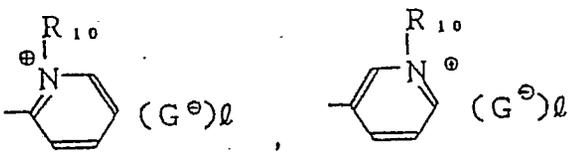


where R_4 and R_5 respectively have the same meanings as R_2 and R_3, provided that R_2 and R_3, R and R′ and R_4 and R_5 may respectively combine to form a ring;

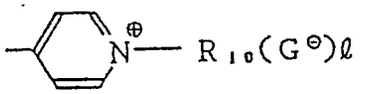


(IV)

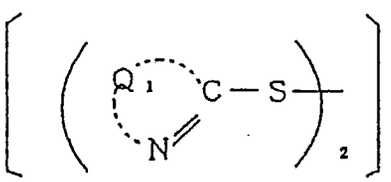
where R_8 and R_9 are each



or

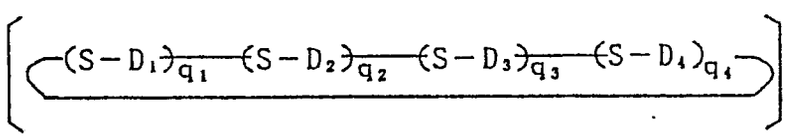


R_{10} is an alkyl group or $-(CH_2)_{n8}SO_3\ominus$ (provided that when R_{10} is $-(CH_2)_{n8}SO_3\ominus$, ℓ is O, and when R_{10} is an alkyl group, ℓ is 1); G⊖ is an anion; and n_8 is an integer of 1 - 6;



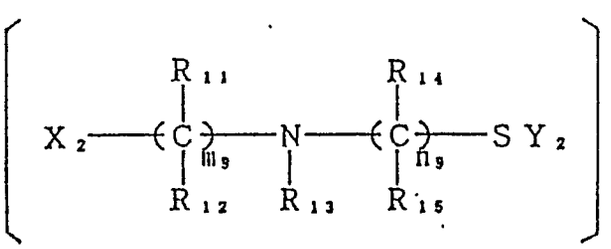
(V)

where Q_1 is the atomic group necessary to form the nitrogenous hetero ring;



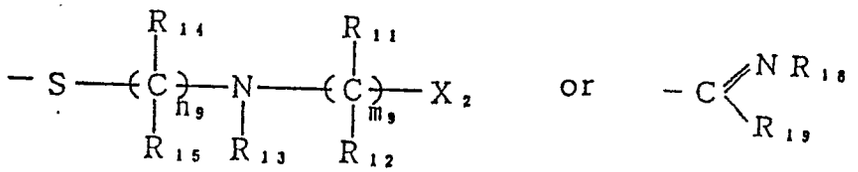
(VI)

where D_1, D_2, D_3 and D_4 are each a simple bond or a hydrocarbon chain; q_1, q_2, q_3 and q_4 are each 0, 1 or 2;



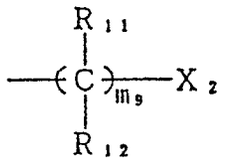
(VII)

where X_2 is a hydrogen atom, R_{16}, -COOM′, -OH, $-SO_3M'$, $-CONH_2$, $-SO_2NH_2$, $-NH_2$, -CN, $-CO_2R_{16}$, $-SO_2R_{16}$, $-OR_{16}$, $-NR_{16}R_{17}$, $-SR_{16}$, $-SO_3R_{16}$, $-NHCOR_{16}$, $-NHSO_2R_{16}$, $-OCOR_{16}$ or $-SO_2R_{16}$;
Y_2 is



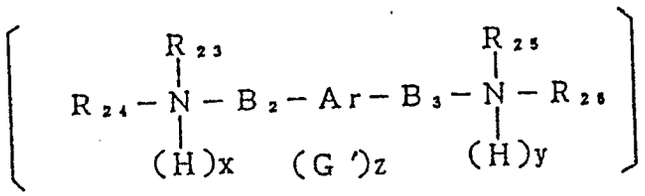
or

m_9 and n_9 are each an integer of 1 - 10; R_{11}, R_{12}, R_{14}, R_{15}, R_{17} and R_{18} are each a hydrogen atom, an alkyl group or an acyl group; R_{13} is a hydrogen atom, an alkyl group, an acyl group or



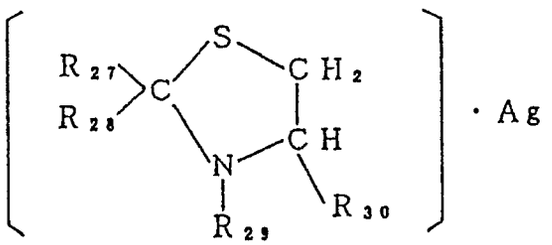
;

R_{16} is an alkyl group; R_{19} is $-NR_{20}R_{21}$, $-OR_{22}$ or $-SR_{22}$; R_{20} and R_{21} are each a hydrogen atom or an alkyl group; R_{22} is the atomic group necessary to form a ring in combination with R_{18}; R_{20} or R_{21} may combine with R_{18} to form a ring; and M′ is a hydrogen atom or a cation;



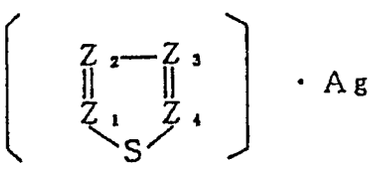
(VIII)

where Ar is an arylene or a divalent organic group containing an arylene group; B_2 and B_3 are each an alkylene group; R_{23}, R_{24}, R_{25} and R_{26} are each a hydroxy-substituted alkyl group; x and y are each 0 or 1; G′ is an anion; and z is 0, 1 or 2;



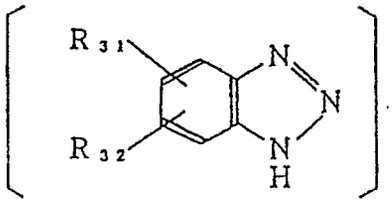
(IX)

where R_{27} and R_{28} are each a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; R_{29} is a hydrogen atom or an alkyl group; R_{30} is a hydrogen atom or a carboxyl group;



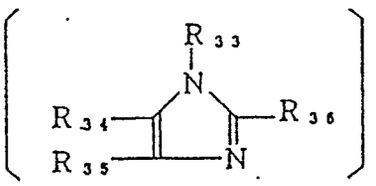
(X)

where Z_1, Z_2, Z_3 and Z_4 are each a carbon atom or a nitrogen atom, and at least one of these is a nitrogen atom;



· Ag (XI)

where R_{31} and R_{32} are each a hydrogen atom or substituent; and



· Ag (XII)

where R_{33}, R_{34}, R_{35} and R_{36} are each a hydrogen atom or a substituent.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in detail.

In the general formula (I), the hetero ring formed by Q and the hetero ring formed by R_1 each includes a condensed hetero ring (e.g. a hetero ring formed by condensing 5- or 6-membered unsaturated rings) and the alkyl group represented by R_1 preferably contains 1 - 5 carbon atoms. The hetero ring formed by Q and the group represented by R_1 include those having substituents such as alkyl, carboxyl, sulfo, acyl, etc.

In the general formula (II), the hetero ring formed by Qo includes a condensed hetero ring (e.g. a hetero ring formed by condensing 5- or 6-membered unsaturated rings) and may have substituents such as alkyl, aryl, carboxyalkyl, alkoxycarbonylalkyl, halogen, vinyl, anilino, acylamino, sulfonamido, etc.

In the general formula (III), the alkyl group represented by R_2, R_3 or R'' and the alkylene group represented by B each preferably contains 1 - 6 carbon atoms, and the acyl group represented by R_2 or R_3 preferably contains 2 - 4 carbon atoms.

The heterocyclic group represented by A or R'' includes a condensed hetero ring (e.g. a hetero ring formed by condensing 5- or 6-membered unsaturated rings), and the group represented by R_2, R_3, A or R'' may contain substituents such as hydroxyl, alkyl, amino, etc.

The group represented by R_8 or R_9 in the general formula (IV) may have a substituent.

In the general formula (V), the hetero ring formed by Q_1 includes a condensed hetero ring (e.g. a hetero ring formed by condensing 5- or 6-membered unsaturated or saturated rings) and may contain substituents such as carboxyl, sulfo, etc.

In the general formula (VI), the hydrocarbon chain represented by D_1 - D_4 may be saturated or unsaturated, and may be exemplified by alkylene and alkenylene, with those having 1 - 8 carbon atoms being preferred. The sulfureous hetero ring includes a condensed hetero ring (e.g. a hetero ring formed by condensing 5- or 6-membered saturated or unsaturated rings) and may contain substituents such as hydroxyalkyl, hydroxyl, carboxyalkyl, etc.

In the general formula (VII), the alkyl group represented by R_{11} - R_{18}, R_{20} or R_{21} preferably contains 1 -6 carbon atoms.

In the general formula (VIII), the arylene group represented by Ar may be exemplified by phenylene, biphenylylene, etc., and examples of the divalent organic group containing an arylene group include the combination of an arylene group and an alkylene group and/or a hetero atom (e.g. oxygen).

The alkylene group represented by B_2 or B_3 and the hydroxy-substituted alkyl group represented by R_{23} - R_{26} preferably contain 1 - 6 carbon atoms.

If Z_1, Z_2, Z_3 or Z_4 in the general formula (X) is a carbon atom, it may contain substituents such as alkylthio, aryl, carboxyalkyl, amino, carboxyalkylthio, arylthio, heterocyclic ring, aryloxy and acyloxy groups, etc.

The substituent represented by R_{31} or R_{32} in the general formula (XI) may be exemplified by an alkyl

group, an alkoxy group, an aryl group, a carboxyl group, a halogen atom, an amino group, a hydroxyl group, a sulfo group, etc.

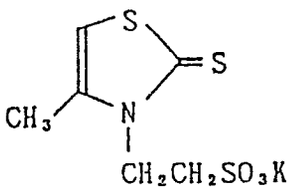
The substituent represented by R_{33} - R_{36} in the general formula (XII) may be exemplified by an alkyl group, an alkoxy group, an amino group, a hydroxyl group, a mercapto group, an acylamino group, a carbamoyl group, etc.

The compounds of the present invention represented by the general formulas (I) - (XII) may be expressed by (B)•Ag.

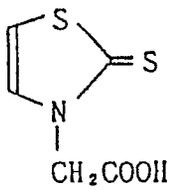
The compounds (B) are illustrated by, but not limited to, the following typical examples.

Illustrative compounds:

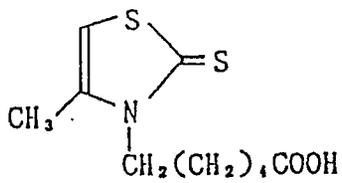
(I - 1)



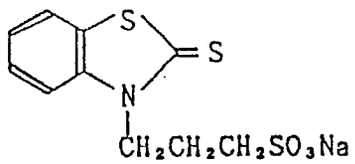
(I - 2)



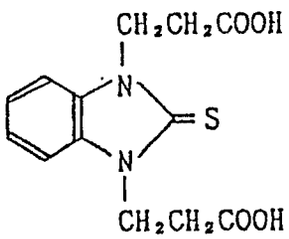
(I - 3)



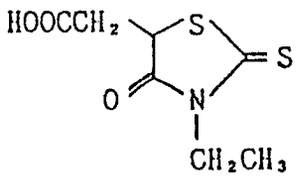
(I - 4)



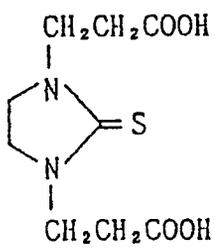
(I - 5)



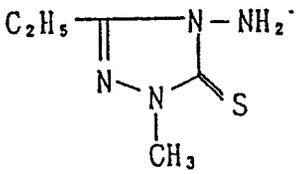
(I - 6)



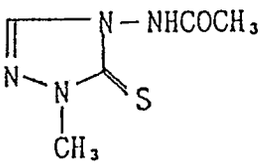
(I - 7)



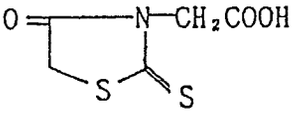
(I - 8)



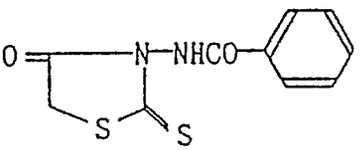
(I - 9)



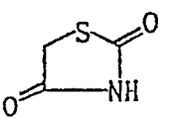
(I - 10)



(I - 11)



(II - 1)



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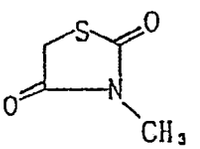
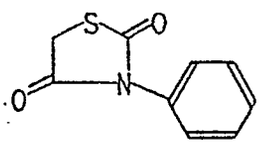
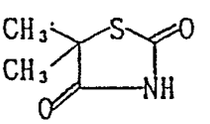


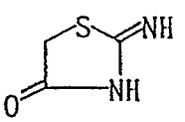
(II - 3)



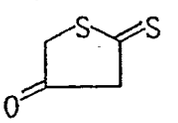
(II - 4)



(II - 5)



(II - 6)



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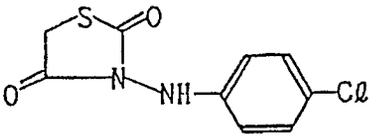

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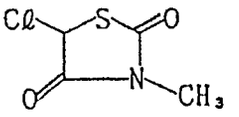

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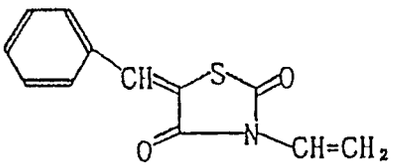

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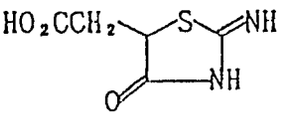

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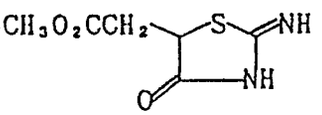

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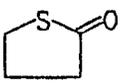

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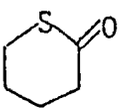

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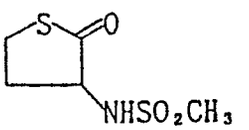

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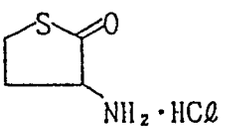

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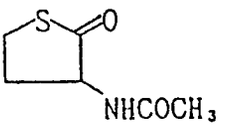

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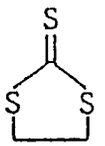

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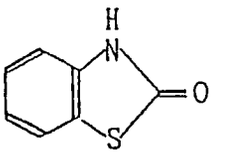

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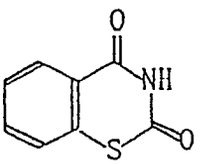

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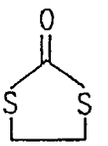

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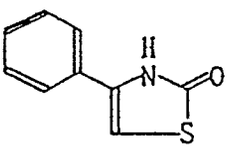

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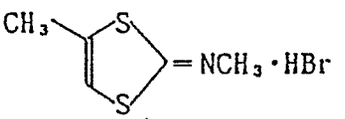

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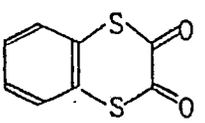

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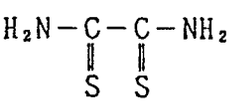

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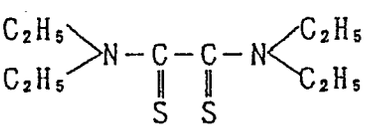

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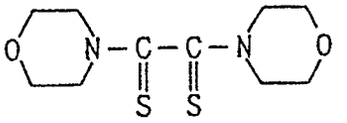

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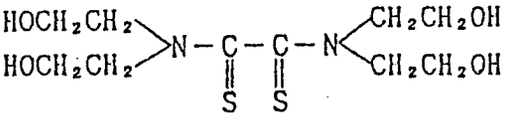

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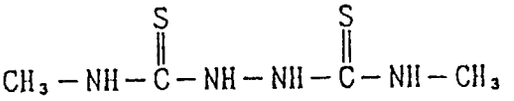

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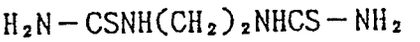

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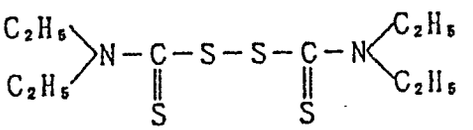

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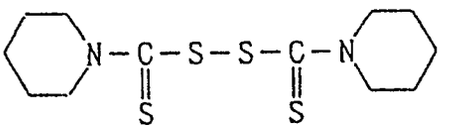

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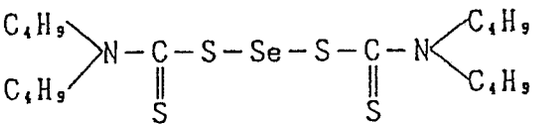

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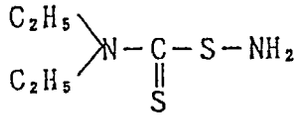

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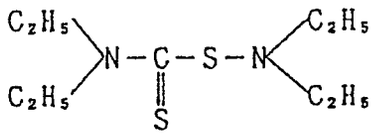

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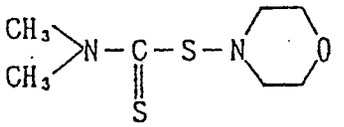

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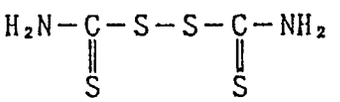

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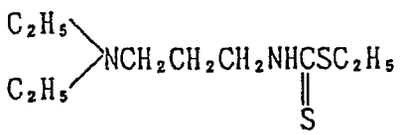

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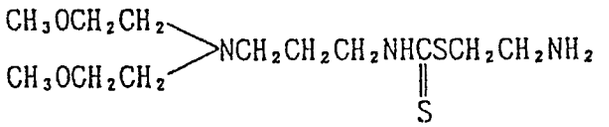

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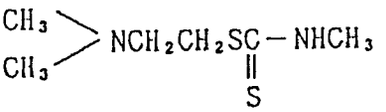

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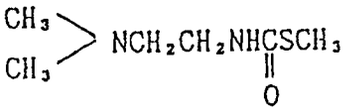

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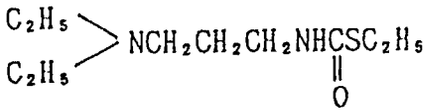

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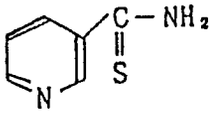

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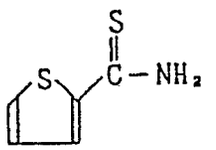

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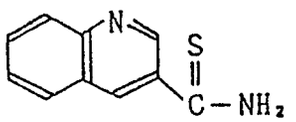

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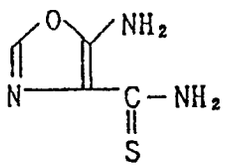

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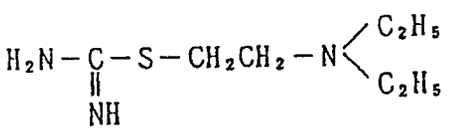

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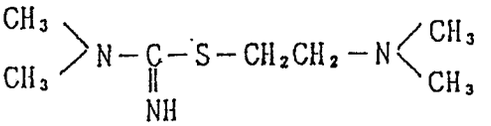

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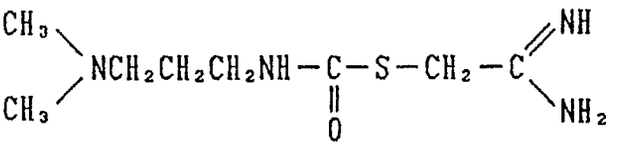

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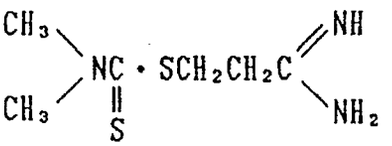

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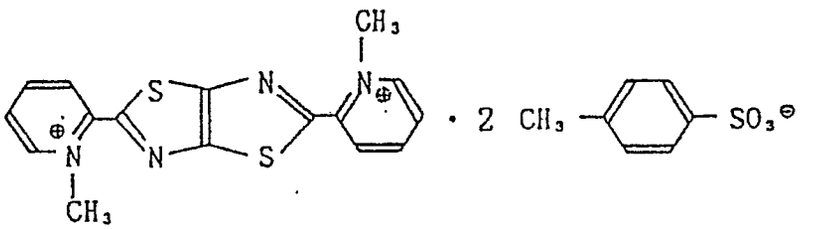

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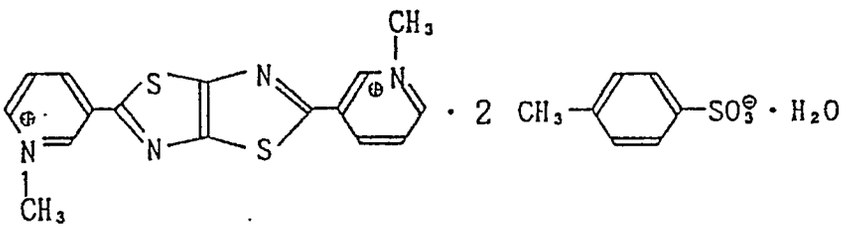

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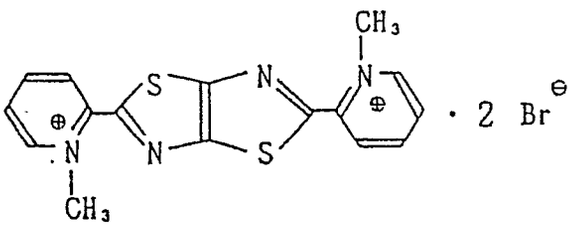

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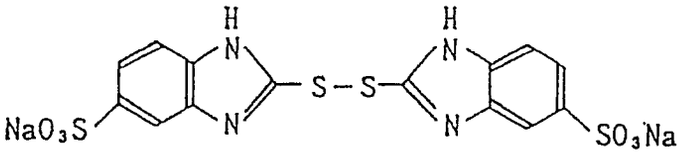

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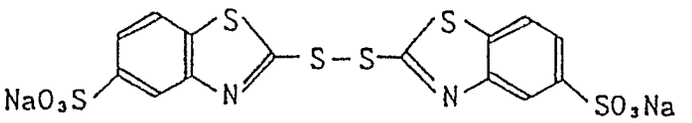

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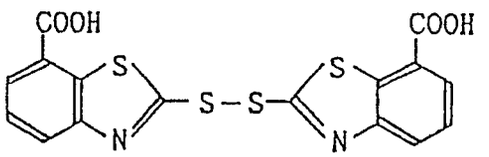

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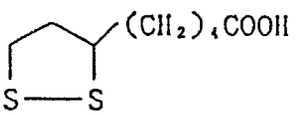
(VI - 2)



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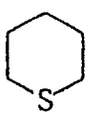

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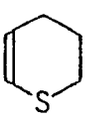

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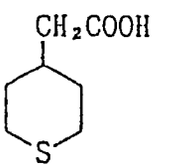

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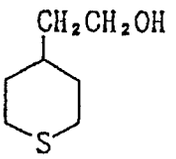

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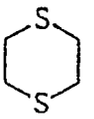

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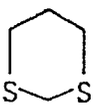

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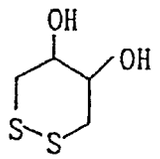

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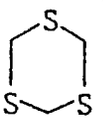

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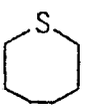

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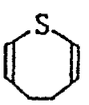

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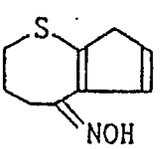

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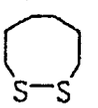

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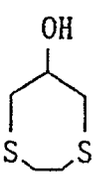

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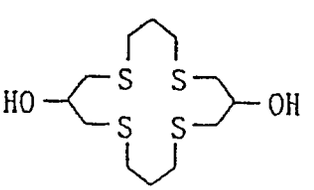

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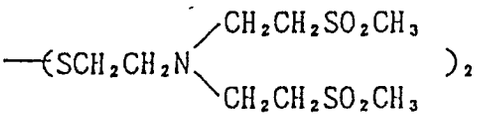

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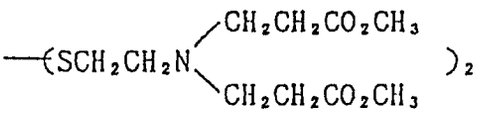

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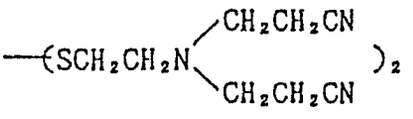

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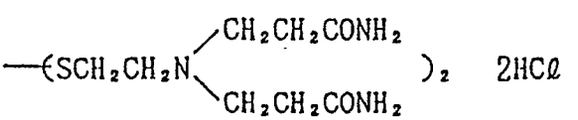

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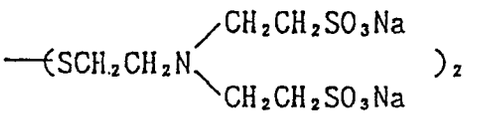

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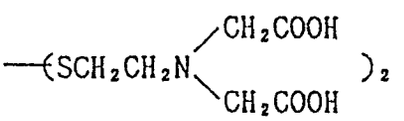

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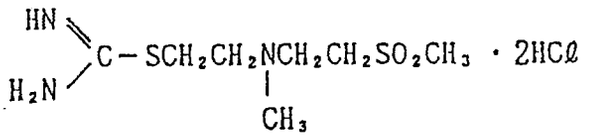

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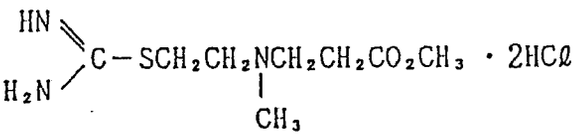

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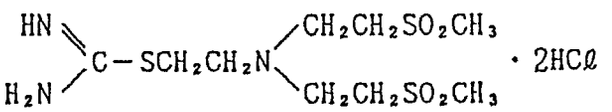

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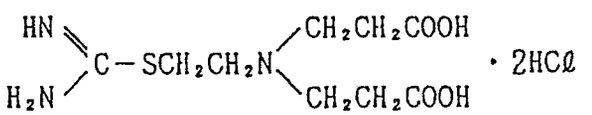

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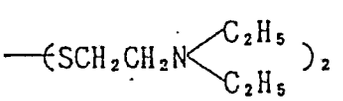

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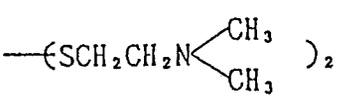

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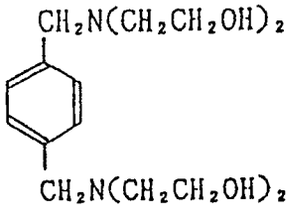

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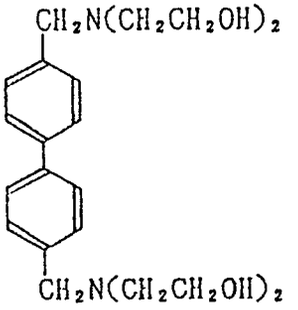

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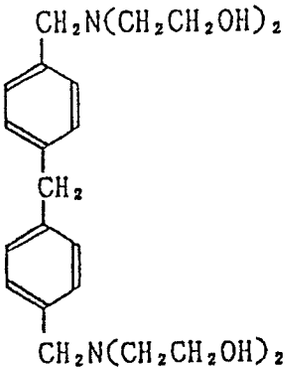

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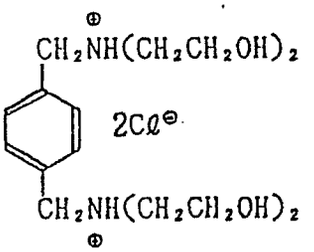

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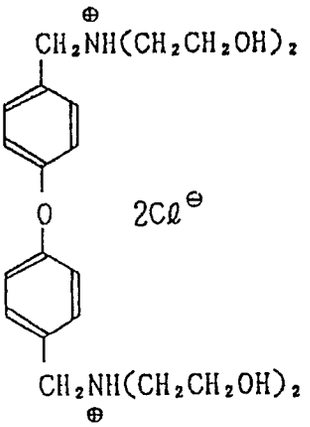

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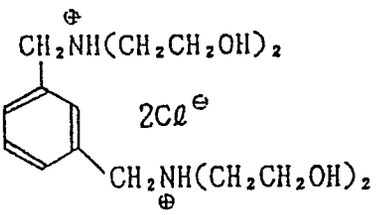

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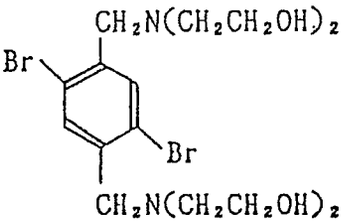

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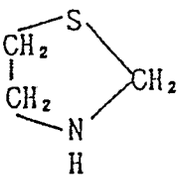

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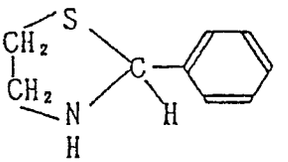

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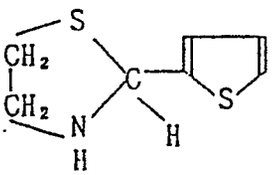

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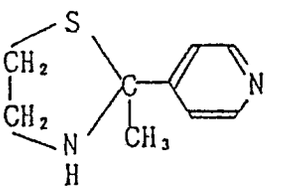

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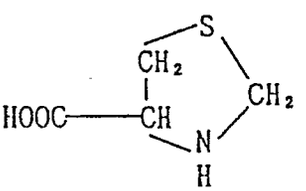

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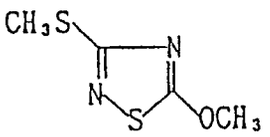

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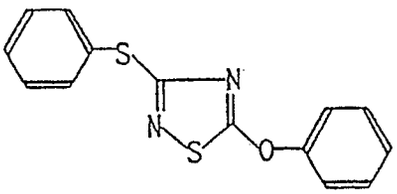

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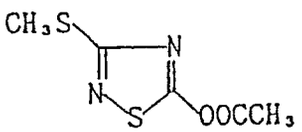

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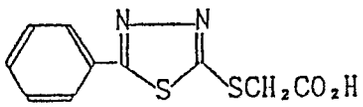

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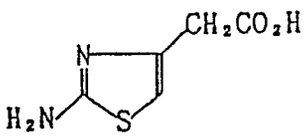

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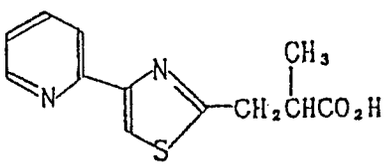
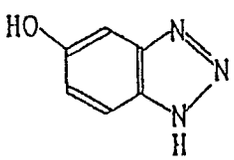


(XI — 1)



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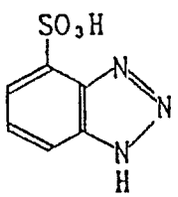

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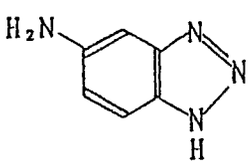

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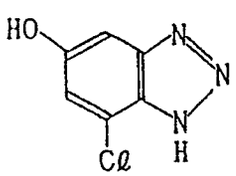

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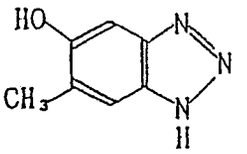

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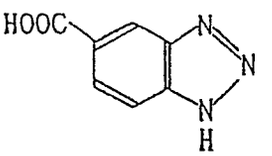

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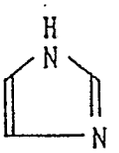

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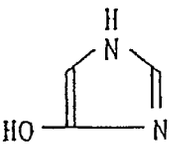

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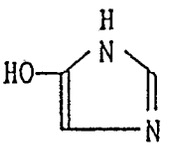

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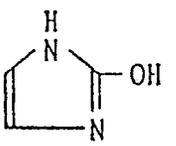

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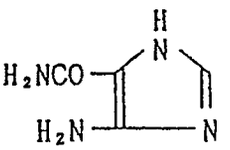

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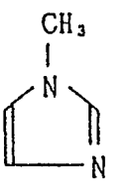

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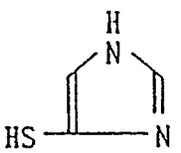

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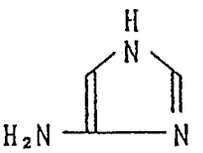


The compounds (B) listed above can be easily synthesized by various known techniques such as those described in British Patent No. 1,138,842, Unexamined Published Japanese Patent Application Nos. 20832/1977, 28426/1978, 95630/1978, 104232/1978, 141632/1978, 17123/1980, 95540/1985, 75352/1986 and 83537/1986, as well as United States Patents 3,232,936, 3,772,020, 3,779,757, and 3,893,858.

The compounds of the present invention can be readily synthesized by mixing aqueous solutions of compounds (B) with an aqueous solution of silver nitrate.

The compounds of the present invention only need be present in the color photographic material of the present invention and they may be incorporated in light-sensitive or non-light-sensitive layers, preferably in non-light-sensitive layers. Most preferably the compounds are incorporated in a non-light-sensitive layer between the support and the light-sensitive layer that is positioned the closest to the support.

The compounds of the present invention are preferably incorporated in amounts ranging from 1×10^{-4}

to 100 g, more preferably from 1×10^{-2} to 1 g, per square meter of the light-sensitive material.

Typical examples of the method for synthesizing the compounds of the present invention are described below. Those compounds are preferably added in the form of a liquid dispersion, so methods for preparing liquid dispersions are also described below.

Synthesis of compound I-2

Rhodanine-3-acetate (19.1 g) was dissolved in 2,000 ml of water and a 10% aqueous solution of silver nitrate (169 g) was added over a period of 15 min. After stirring for an additional 2 h, the resulting white crystal was recovered by filtration, washed with 2,000 ml of water and vacuum-dried to obtain the end compound in an amount of 24.1 g.

Preparation of liquid dispersion

To 14.9 g or compound I-2 synthesized above, 10 ml of 5% Alkanol XC (Du Pont) and 300 ml of water were added and the mixture was treated with a ball mill for 12 h to obtain a liquid dispersion.

Synthesis of compound II-2

4-Sulfobenzotriazole (31 g) was dissolved in 1,000 ml of water and 338 g of a 10% aqueous solution of silver nitrate was added over a period of 30 min. After stirring for an additional 2 h, the resulting white crystal was recovered by filtration, washed with 2,000 ml of water and vacuum-dried to obtain the end compound (4-sulfobenzotriazole silver) in an amount of 46.3 g.

Preparation of liquid dispersion

To 20 g of 4-sulfobenzotriazole, 10 ml of 5% Alkanol XC (Du Pont) and 400 ml of water were added and the mixture was treated with a ball mill for 12 h to obtain a milky white liquid dispersion.

The silver halide emulsion to be used in the present invention may employ silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide, silver chloride and any other silver halides that are commonly used in silver halide emulsions.

The silver halide grains used in the silver halide emulsion may have a uniform compositional distribution in the bulk of the grains, or they may be core/shell grains having different silver halide compositions in the interior and the surface layers of the grains.

The silver halide grains may be of a type that forms a latent image predominantly on the surface, or of a type that forms a latent image predominantly in the bulk of the grains.

The silver halide emulsion may have any grain size distribution. It may have a broad grain size distribution (silver halide emulsions of this type are generally referred to as "polydispersed emulsions"), or emulsions having a narrow grain size distribution (generally referred to as "monodispersed emulsions") may be used either on their own or as admixtures. If desired, a polydispersed emulsion may be used in admixture with a monodispersed emulsion.

Separately prepared two or more silver halide emulsions may be used in admixture.

The silver halide emulsion to be used in the present invention may be chemically sensitized or they may be spectrally sensitized to a desired wavelength range by treatment with sensitizers.

Antifoggants, stabilizers and other additives may be added to the silver halide emulsion. Gelatin is advantageously used as a binder in said emulsion.

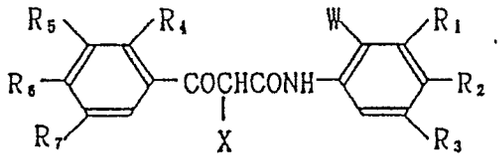
Emulsion layers and other hydrophilic colloidal layers may be hardened and they may incorporate plasticizers or dispersions (latices) of synthetic polymers that are either insoluble or slightly soluble in water.

Couplers are used in the emulsion layers of the color light-sensitive material. Also usable are competitive couplers which are capable of color correction, as well as compounds that couple with the oxidation product of developing agents to release photographically useful fragments such as development accelerators, bleach accelerators, developers, silver halide solvents, toning agents, hardeners, foggants, anti-foggants, chemical sensitizers, spectral sensitizers, desensitizers, etc.

Known acylacetanilide couplers may preferably be used as yellow-dye forming couplers. Among

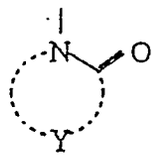
acylacetanilide couplers, benzoylacetanilide and pivaloylacetanilide compounds are advantageous.

Compounds represented by the following general formula (YB-1) are particularly preferred for use as yellow-dye forming couplers in the present invention:



(YB-1)

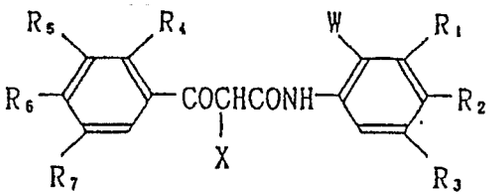
where R_1 - R_7 and W are each a hydrogen atom or a substituent; preferably, R_1, R_2 and R_3, which may be the same or different, each represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alkoxy group, an acylamino group, a carbamoyl group, an alkoxycarbonyl group, a sulfonamido group or a sulfamoyl group; R_4, R_5, R_6 and R_7, which may be the same or different, each preferably represents a hydrogen atom, an alkyl group, an alkoxy group, an aryloxy group, an acylamino group or a sulfonamide group; W is preferably a halogen atom, an alkyl group, an alkoxy group, an aryloxy group or a dialkylamino group; X is a hydrogen atom or a group that can be eliminated, and a preferred group that can be eliminated is represented by the following general formula (YB-II):



(YB-II)

where Y is a group of the non-metallic atoms necessary to form a 5- or 6-membered ring.

The benzoylacetanilide yellow couplers may be illustrated by, but not limited to, the following examples.



Compound No.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	W	X
YB-1	H	H	(7)	H	H	(4)	H	(1)	(16)
YB-2	H	H	(7)	H	H	(4)	H	(1)	(17)
YB-3	H	H	(8)	H	H	H	H	(1)	(18)
YB-4	H	H	(8)	H	H	H	H	(4)	(19)
YB-5	H	H	(6)	(2)	H	H	H	(4)	(20)
YB-6	H	H	(9)	H	H	(4)	H	(1)	(21)
YB-7	H	H	(11)	H	(10)	(4)	H	(4)	(22)
YB-8	H	H	H	H	H	H	(7)	(4)	(23)
YB-9	H	H	(12)	H	H	(4)	H	(1)	(24)
YB-10	H	H	(13)	H	H	H	H	(1)	(25)
YB-11	H	H	(14)	H	H	(4)	H	(1)	(26)
YB-12	H	H	(15)	H	H	(4)	H	(4)	(27)
YB-13	H	H	H	H	H	(4)	H	(4)	H
YB-14	H	H	H	H	H	(5)	H	(1)	(28)
YB-15	H	H	(6)	H	H	(4)	H	(1)	(17)
YB-16	H	H	(6)	H	H	(4)	H	(1)	(29)
YB-17	H	H	(7)	H	H	(4)	H	(1)	(29)
YB-18	H	H	H	H	H	H	(7)	(4)	H
YB-19	H	H	(30)	(31)	H	H	H	(1)	H
YB-20	H	H	(11)	H	H	(32)	H	(4)	(33)
YB-21	H	H	(34)	H	H	(4)	H	(1)	(35)

(1) $-Cl$

(2) $-CH_3$

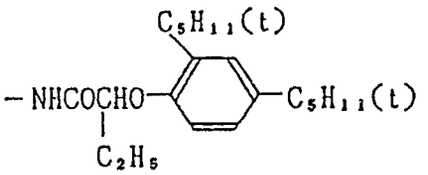
(3) $-C_{18}H_{37}$

(4) $-OCH_3$

(5) $-NHCOC_{17}H_{35}$

(6) $-COOC_{12}H_{25}$

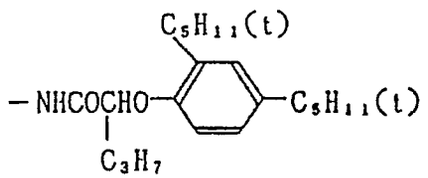
(7)



(8) $-COOCHCOOC_{12}H_{25}$ (CH$_3$ on the CH)

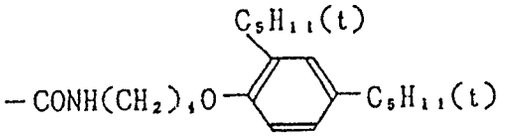
(9) $-NHCOCHCH_2SO_2C_{12}H_{25}$ (CH$_3$ on the CH)

(10)



(11) $-SO_2N(CH_3)_2$

(12)



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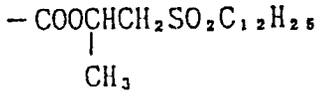

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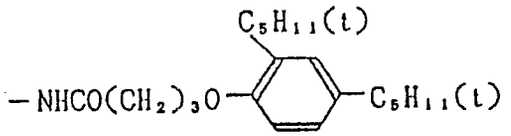

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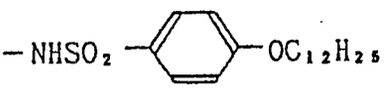

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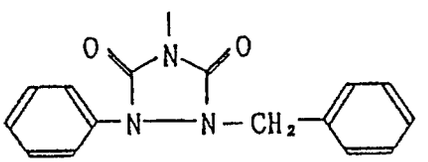

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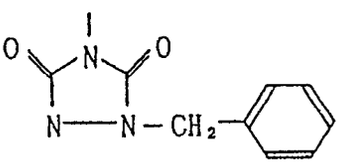

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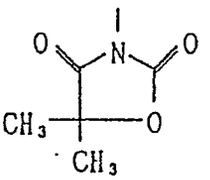

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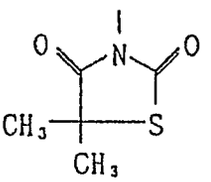

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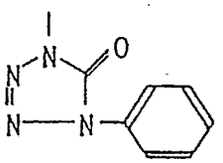

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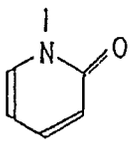

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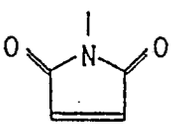

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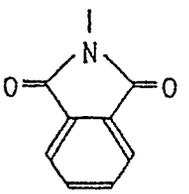

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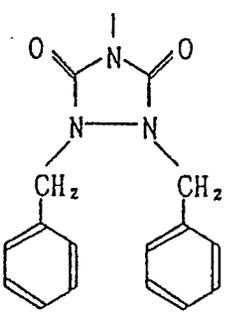

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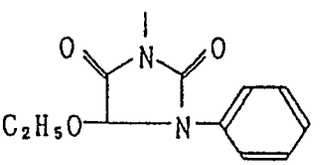

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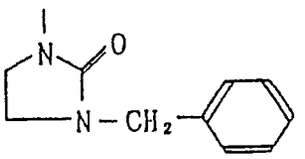

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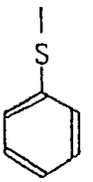

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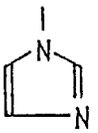

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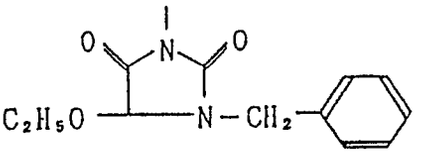

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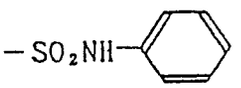

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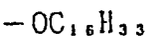
(32)



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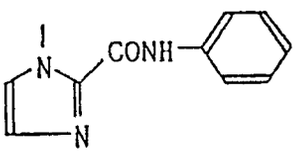

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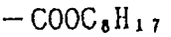

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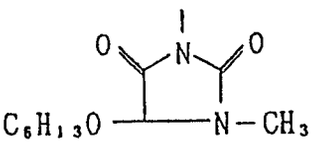


These benzoylacetanilide yellow couplers that can be used in the present invention include those which are described in United States Patent 3,725,072, 3,891,445, Japanese Patent Publication No. 10783/1976, as well as Unexamined Published Japanese Patent Application Nos. 73147/1973, 6341/1975, 102636/1976,115219/1977, 159163/1984 and 174838/1984, and they can be synthesized by the methods described in these patents.

Two or more benzoylacetanilide yellow couplers may be used in the present invention and, if desired, they may be used in combination with other yellow couplers.

Yellow couplers can be incorporated in the photographic material by various methods depending upon the physical properties (e.g. solubility) of the yellow coupler to be incorporated. To mention a few, they may be incorporated by an oil-in-water emulsion dispersion method using water-insoluble high-boiling point organic solvents, an alkali dispersion method in which they are added in the form of an alkaline solution, a latex dispersion method, and a solid dispersion method in which they are added directly as fine solids.

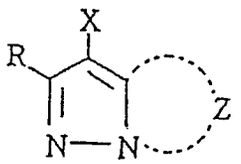
The yellow couplers are incorporated in a total amount that typically ranges from 1.0×10^{-3} to 1.0

mole, preferably from 5.0×10^{-3} to 8.0×10^{-1} moles, per mole of silver halide.

The benzoylacetanilide yellow couplers to be used in the present invention are typically incorporated in blue-sensitive silver halide emulsion layers, but depending on a specific object, they may be incorporated in silver halide emulsion layers having sensitivity to light other than blue, such as in green- or red-sensitive emulsion layers.

Magenta-dye forming couplers that can be used in the present invention include 5-pyrazolone couplers, pyrazoloazole couplers, pyrazolobenzimidazole couplers, open-chain acylacetonitrile couplers, indazole couplers, etc.

Compounds represented by the following general formula (M-I) are particularly preferred for use as magenta-dye forming couplers in the present invention:



(M-I)

where Z is a group of the non-metallic atoms necessary to form the nitrogenous heterocyclic ring which may contain a substituent; X is a hydrogen atom or a group capable of leaving upon reaction with the oxidation product of a color developing agent; and R is a hydrogen atom or a substituent.

While the substituent represented by R is not limited in any particular way but typical examples are alkyl, aryl, anilino, acylamino, sulfonamido, alkylthio, arylthio, alkenyl, cycloalkyl group. Other examples of the substituent R include: a halogen atom; groups such as cycloalkenyl, alkynyl, hetero ring, sulfonyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocycloxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imido, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkoxycarbonyl, aryloxycarbonyl and heterocyclic thio; as well as residues such as spiro compound residue and bridged hydrocarbon compound residue.

The alkyl group represented by R preferably contains 1 - 32 carbon atoms and it may be straight-chained or branched.

A preferred example of the aryl group represented by R is a phenyl group.

The acylamino group represented by R may be exemplified by alkylcarbonylamino, arylcarbonylamino, etc.

The sulfonamido group represented by R may be exemplified by alkylsulfonylamino, arylsulfonylamino, etc.

The alkyl portion of the alkylthio group represented by R, as well as the aryl portion of the arylthio group also represented by R may be exemplified by the alkyl and aryl groups mentioned above in the definition of R.

Preferred examples of the alkenyl group represented by R are those which have 2 - 32 carbon atoms, and preferred examples of the cycloalkyl group represented by R are those which have 3 - 12 carbon atoms, with those having 5 - 7 carbon atoms being particularly preferred. The alkenyl group may be straight-chained or branched.

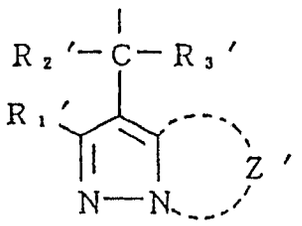
Preferred examples of the cycloalkenyl group represented by R are those which have 3 - 12 carbon atoms, with those having 5 - 7 carbon atoms being particularly preferred.

Other examples of R are listed below:

sulfonyl groups such as alkylsulfonyl and arylsulfonyl;
sulfinyl groups such as alkylsulfinyl and arylsulfinyl;
phosphonyl groups such as alkylphosphonyl, alkoxyphosphonyl, aryloxyphosphonyl and arylphosphonyl;
acyl groups such as alkylcarbonyl and arylcarbonyl;
carbamoyl groups such as alkylcarbamoyl and arylcarbamoyl;
sulfamoyl groups such as alkylsulfamoyl and arylsulfamoyl;
acyloxy groups such as alkylcarbonyloxy and arylcarbonyloxy;
carbamoyloxy groups such as alkylcarbamoyl and arylcarbamoyloxy;
ureido groups such as alkylureido and arylureido;
sulfamoylamino groups such as alkylsulfamoylamino and arylsulfamoylamino;
heterocyclic groups, preferably those which are 5- to 7-membered as exemplified specifically by 2-furyl, 2-thienyl, 2-pyrimidinyl and 2-benzothiazolyl;
heterocycloxy groups, preferably those having 5- to 7-membered hetero rings as exemplified by 3,4,5,6-

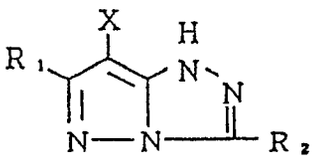
tetrahydropyranyl-2-oxy and 1-phenyltetrazol-5-oxy;
heterocyclic thio groups, preferably those which are 5- to 7-membered as exemplified by 2-pyridylthio, 2-benzothiazolylthio, 2,4-diphenoxy-1,3,5-triazole-6-thio;
siloxy groups such as trimethylsiloxy, triethylsiloxy and dimethylbutylsiloxy;
imido groups such as succinimido, 3-heptadecylsuccinimido, phthalimido and glutarimido;
spiro compound residues such as spiro[3.3]heptan-1-yl; and
bridged hydrocarbon compound residues such as bicyclo[2.2.1]heptan-1-yl; tricyclo[3.3.1.1^{37}]decan-1-yl, and 7,7-dimethyl-bicyclo-[2.2.1]heptan-1-yl.

Examples of the group X which is capable of leaving upon reaction with the oxidation product of color developing agents include: a halogen atom (e.g. Cl, Br or F), and groups such as alkoxy, aryloxy, heterocycloxy, acyloxy, sulfonyloxy, alkoxycarbonyloxy, aryloxycarbonyl, alkyloxalyloxy, alkoxyoxalyloxy, alkylthio, arylthio, heterocyclic thio, alkyloxythiocarbonylthio, acylamino, sulfonamide, a nitrogenous hetero ring formed with the intermediary of N atom, alkyloxycarbonylamino, aryloxycarbonylamino, carboxyl, and

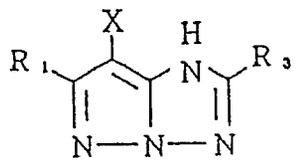


(where R_1' has the same meaning as R; Z' has the same meaning as Z; R_2' and R_3' are each a hydrogen atom, an aryl group, an alkyl group or a heterocyclic group). A preferred example of X is a halogen, with a chlorine atom being particularly preferred. Examples of the nitrogenous hetero ring formed by Z or Z' include pyrazole, imidazole, triazole and tetrazole rings, and the substituent that may be possessed by these rings may be exemplified by those which were listed in the definition of R.

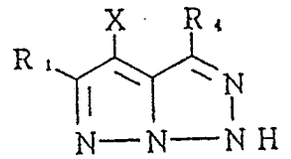
The compound represented by the general formula (M-1) may be represented more specifically by the following formulas (M-II) to (M-VII):



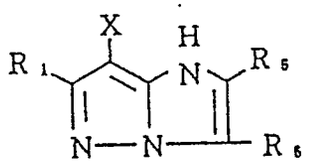
(M-II)



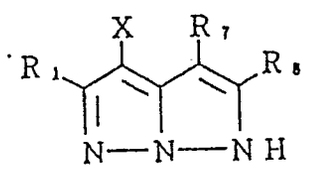
(M-III)



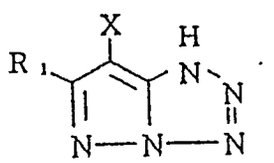
(M-IV)



(M-V)



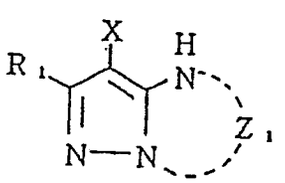
(M-VI)



(M-VII)

In the general formulas (M-II) to (M-VII), R_1 - R_8 and X have the same meanings as already defined for R and X.

Among the compounds represented by the general formula (M-I), those which are represented by the following general formula (M-VIII) are particularly preferred:



(M-VIII)

where R_1, X and Z_1 have the same meanings as R, X and Z in the general formula (M-I).

Among the magenta couplers represented by the general formulas (M-II) to (M-VII), magenta couplers represented by the general formula (M-II) are particularly preferred.

The substituents R and R_1 on the hetero rings described above are most preferably represented by the following general formula (M-IX):

$R_9 - CH_2 -$ (M-IX)

where R_9 has the same meaning as already defined for R.

A preferred example of R_9 is a hydrogen atom or an alkyl group.

The substituent optionally possessed by the ring formed by Z in the general formula (M-I) and the ring formed by Z_1 in the general formula (M-VIII), and R_2 - R_8 in the general formulas (M-II) to (M-VI) are preferably represented by the following general formula (M-X):

$-R^1 - SO_2 - R^2$ (M-X)

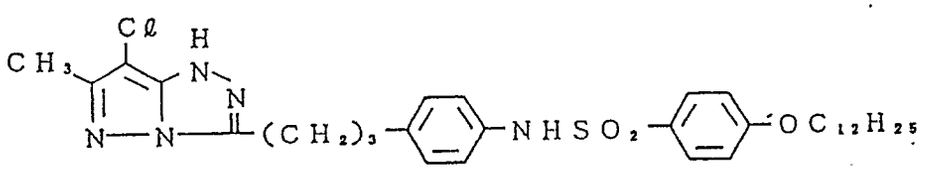
where R^1 is an alkylene group, and R^2 is an alkyl, cycloalkyl or aryl group.

The alkylene group represented by R^1 preferably contains 2 or more carbon atoms, more preferably 3 to 6 carbon atoms, in the straight-chained portion, and it may be either straight-chained or branched.

The cycloalkyl group represented by R^2 is preferably 5- or 6-membered.

Typical examples of the compounds of the present invention are specifically listed below.

M-1



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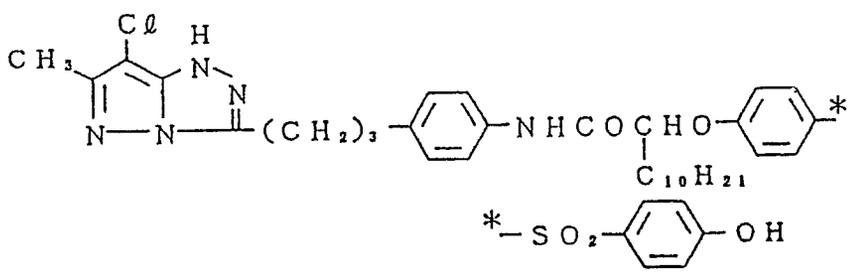

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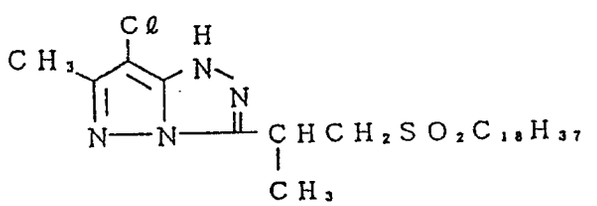

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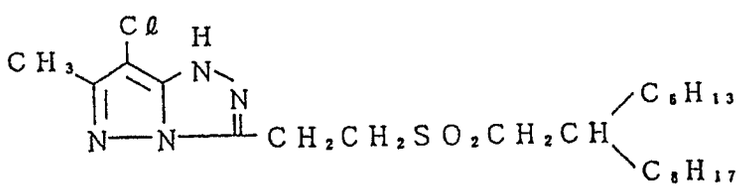

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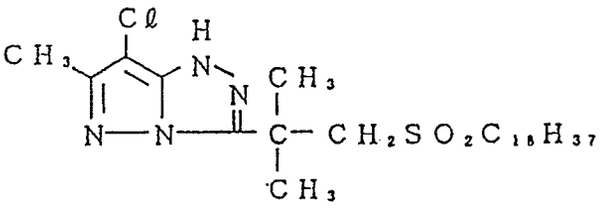

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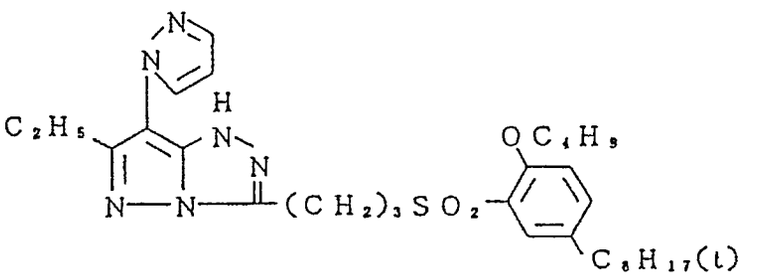

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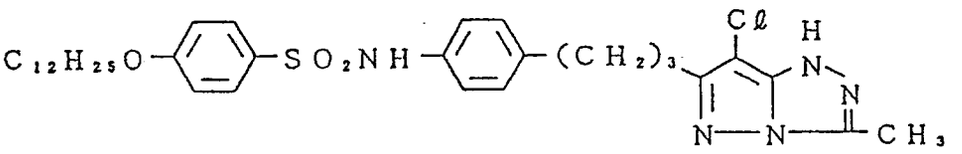

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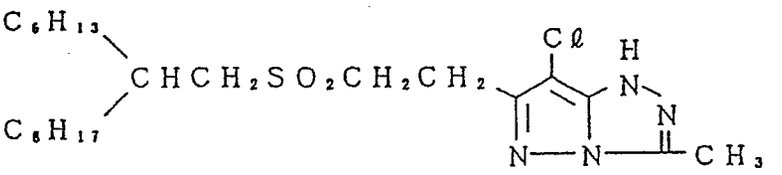

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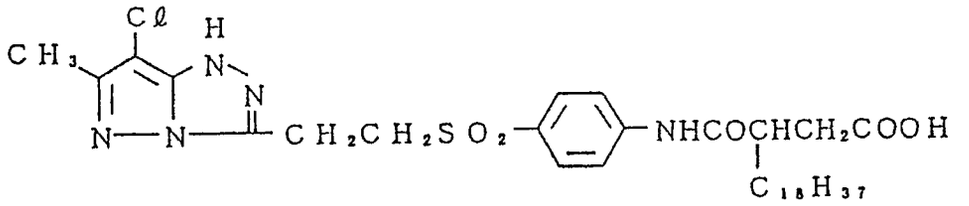

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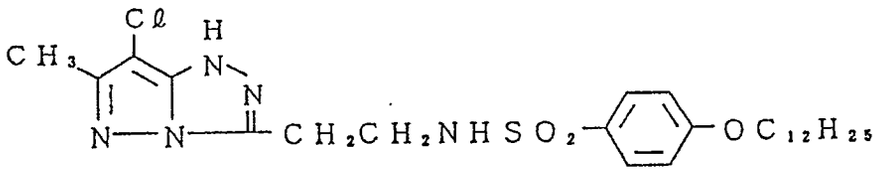

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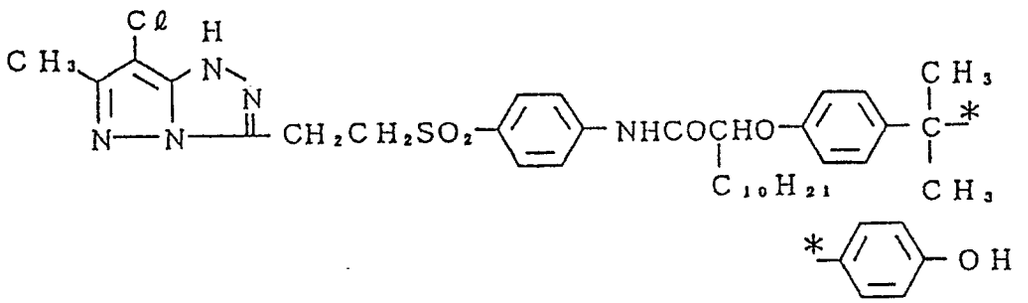

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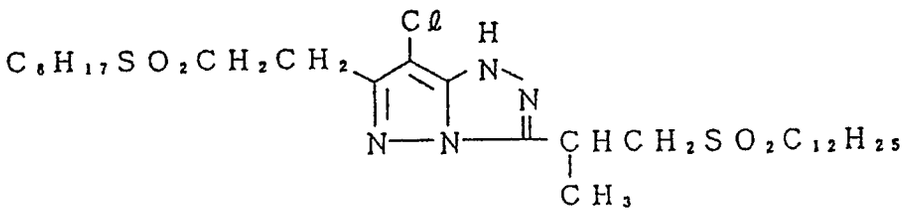

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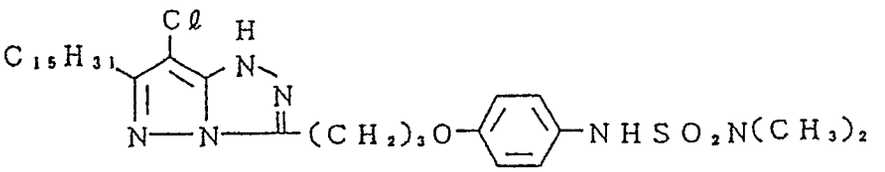

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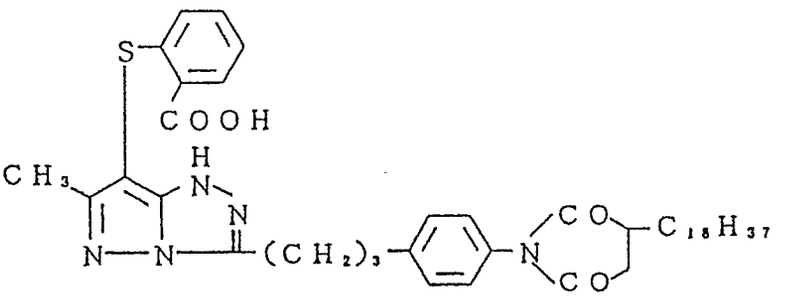

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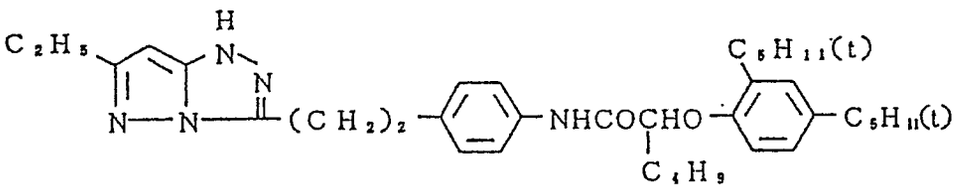

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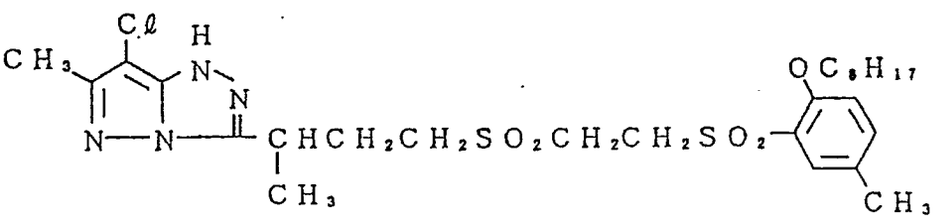

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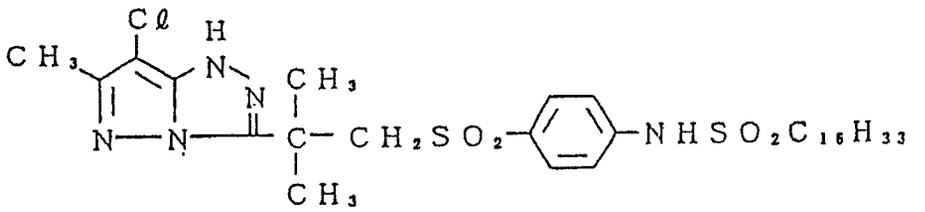

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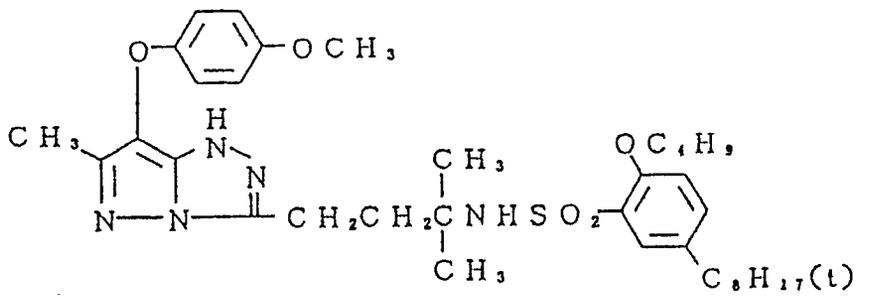

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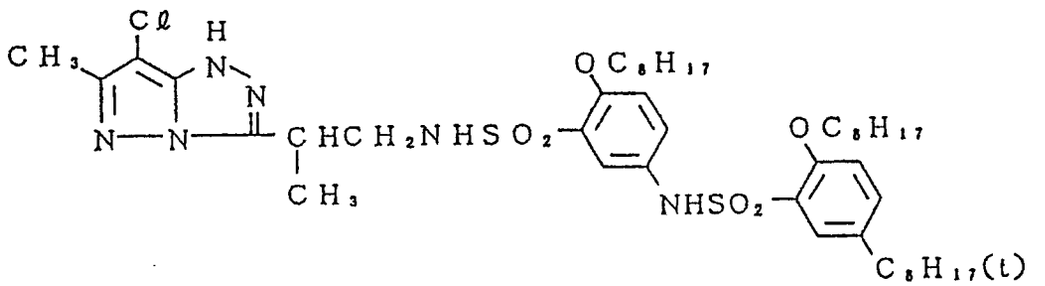

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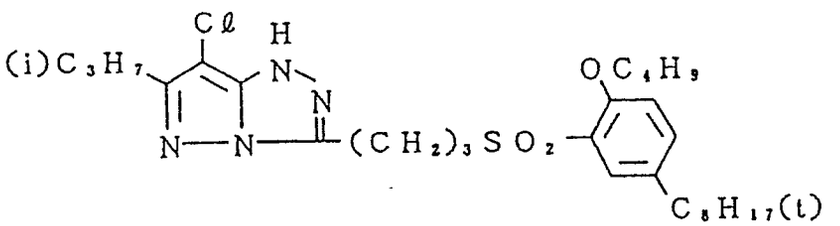

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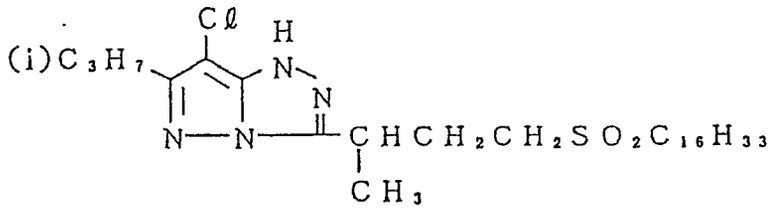

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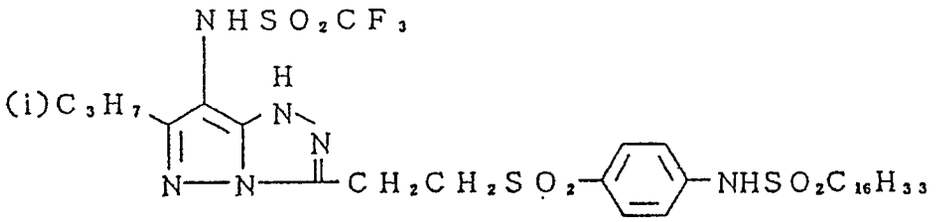

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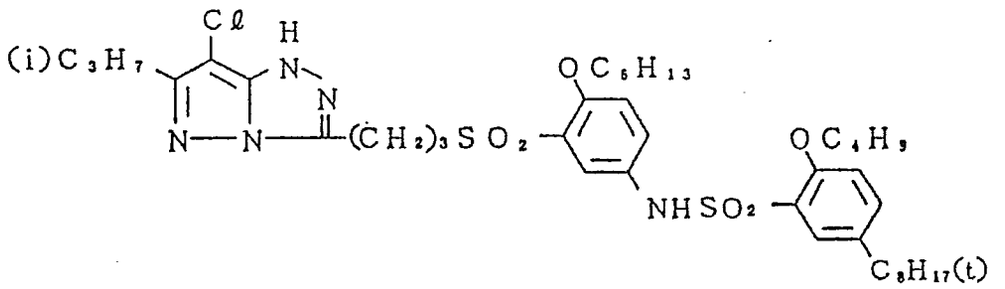

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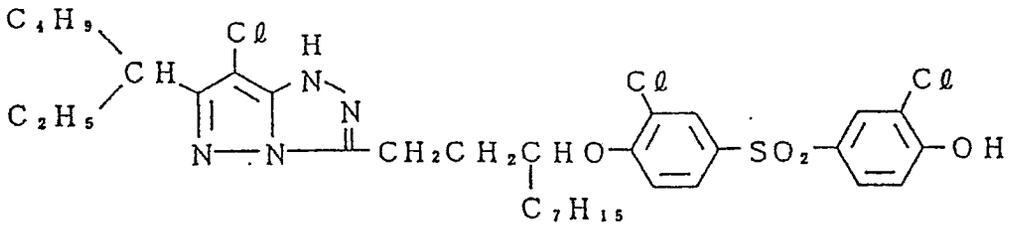

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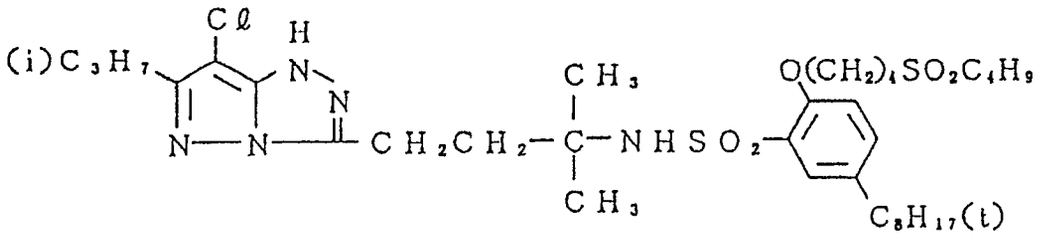

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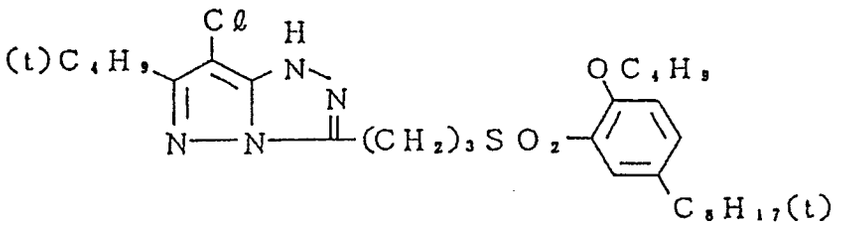

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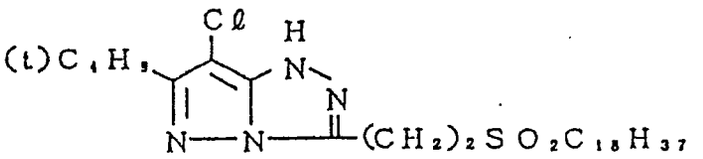

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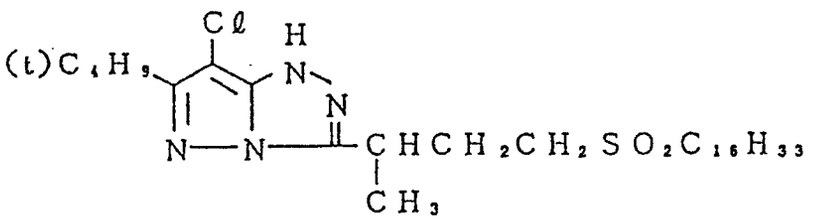

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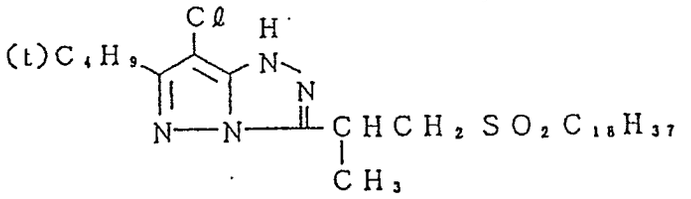

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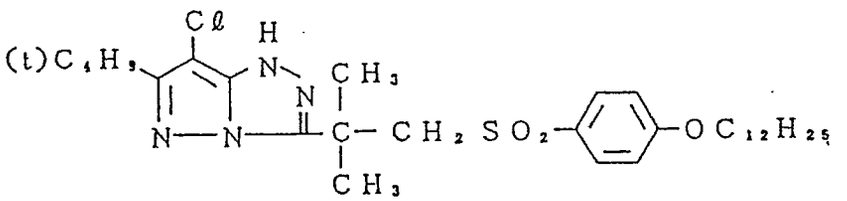

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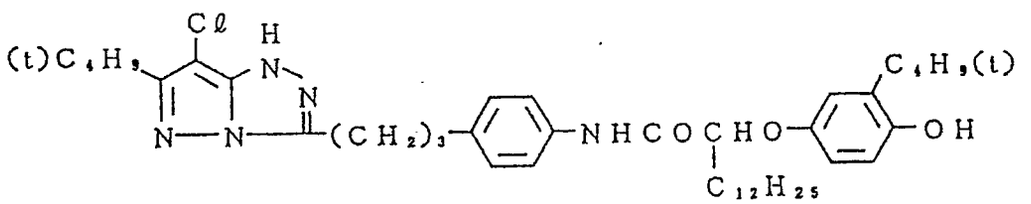

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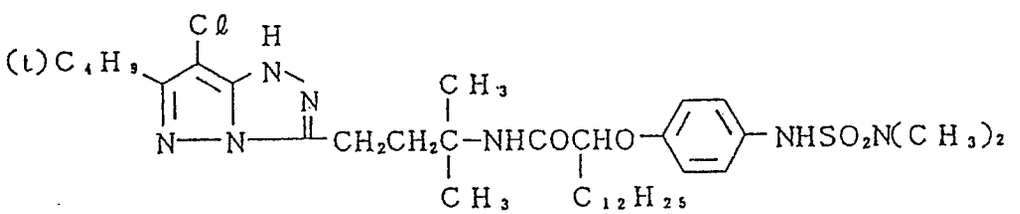

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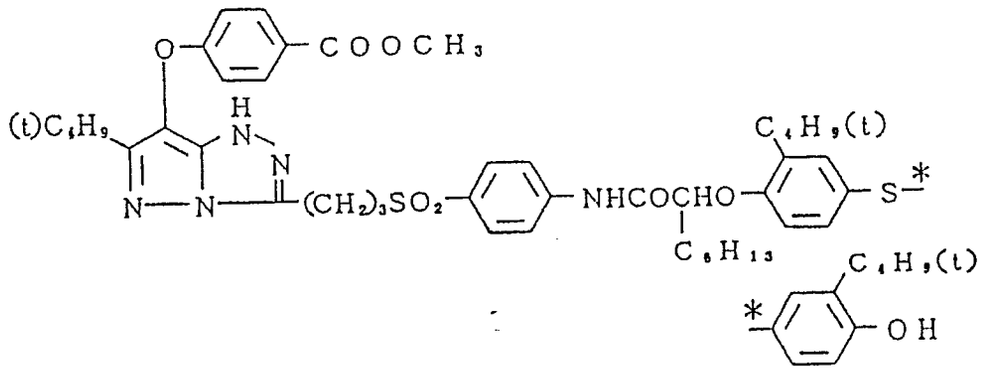

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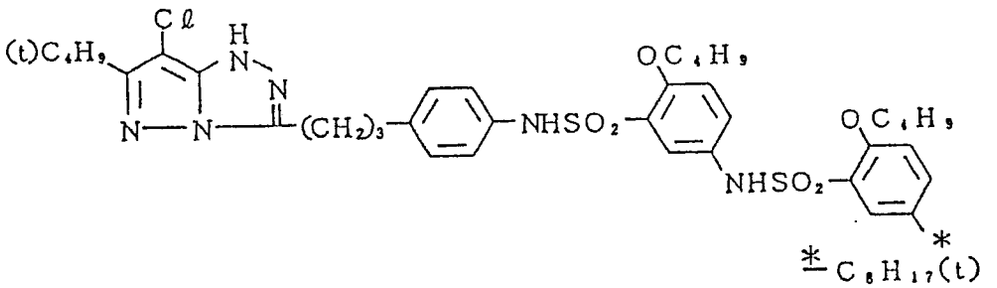

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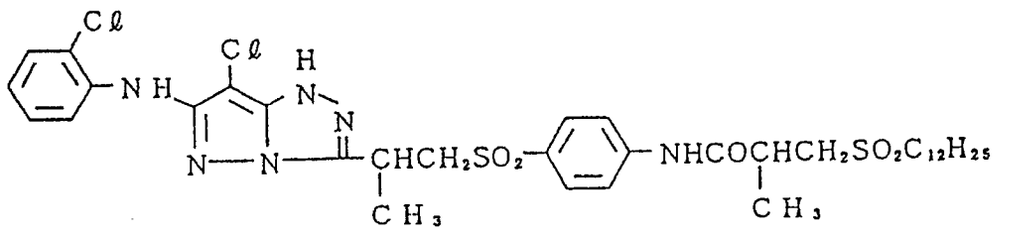

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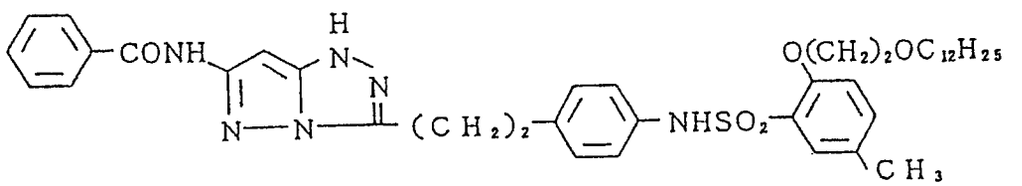

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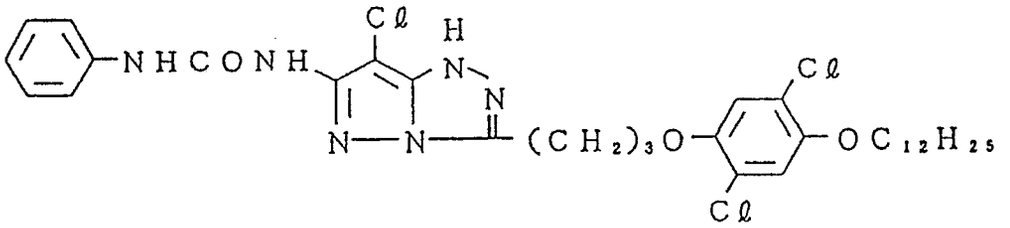

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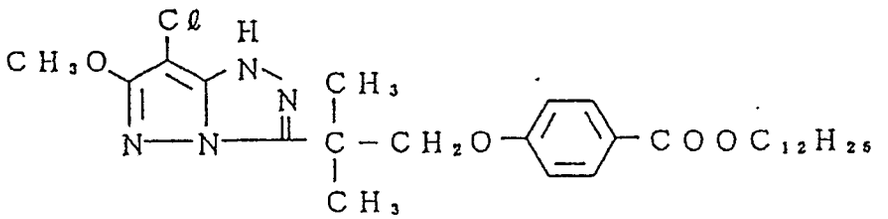

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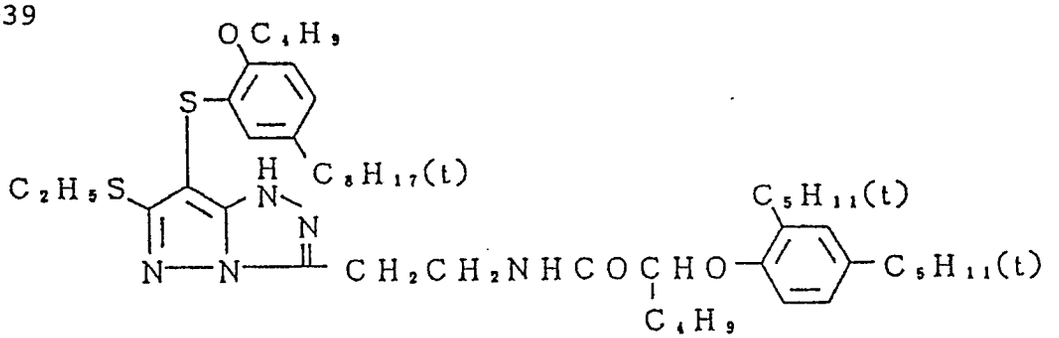

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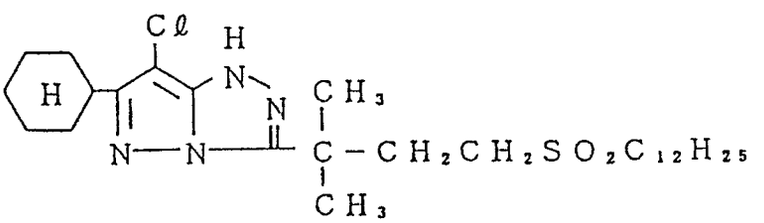

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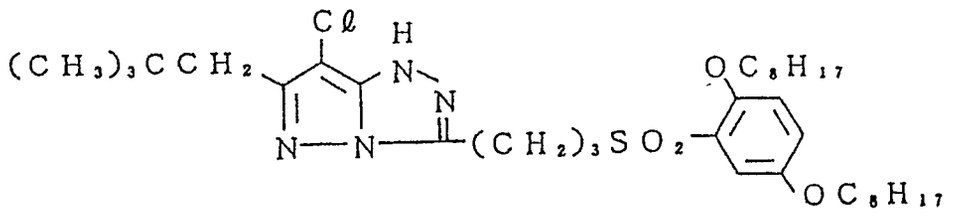

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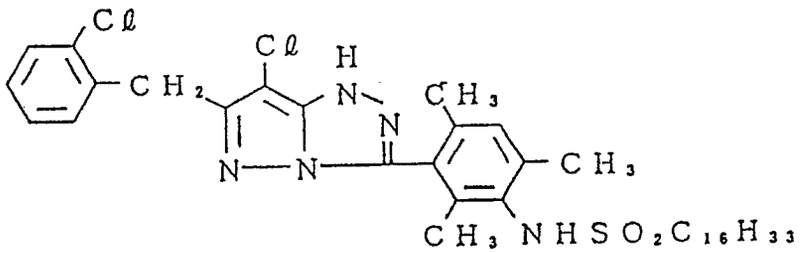

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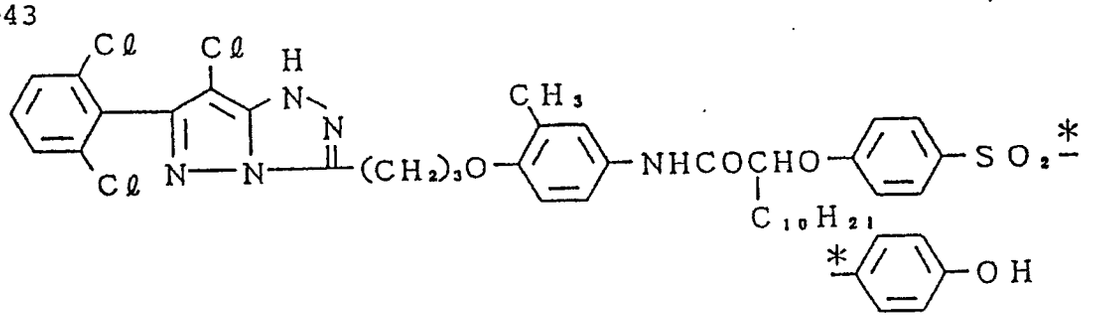

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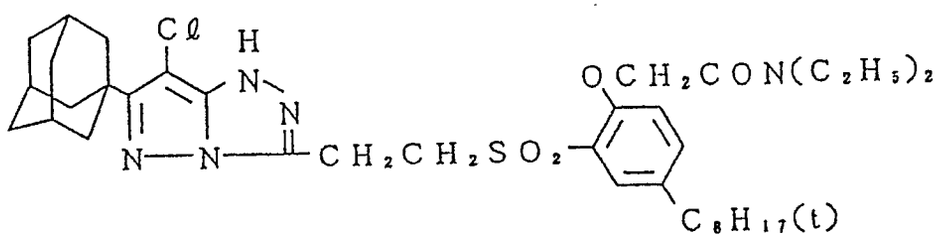

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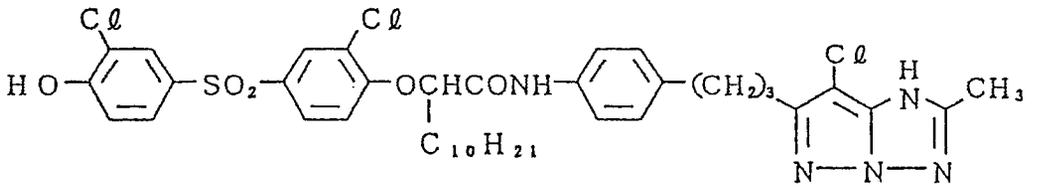

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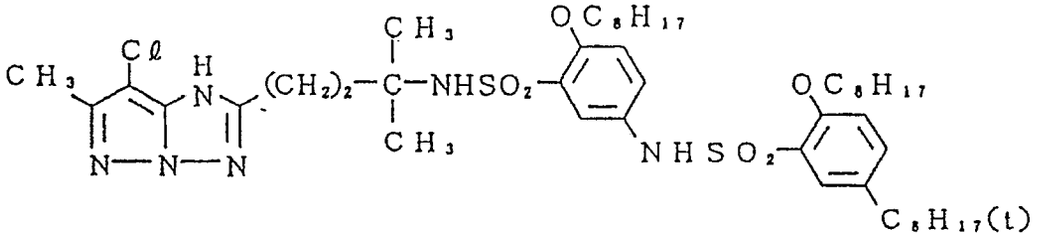

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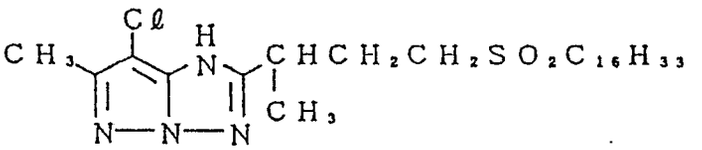

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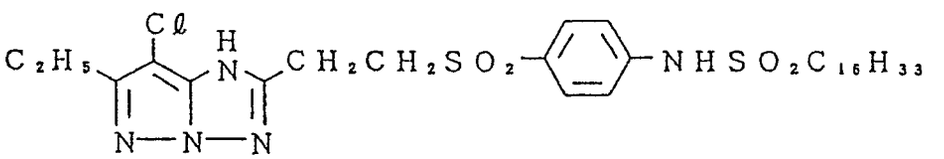

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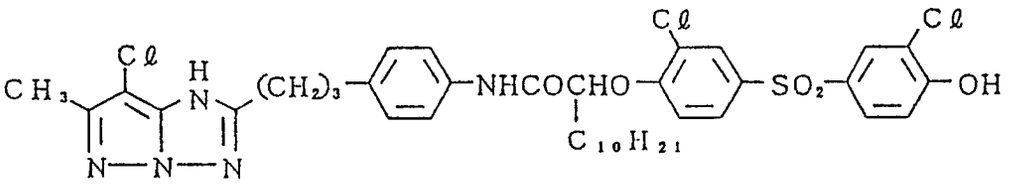

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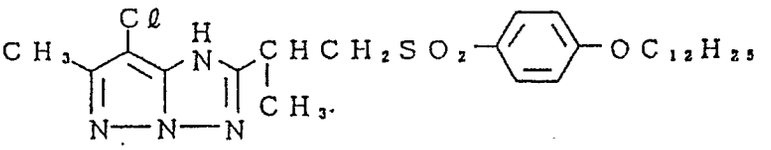

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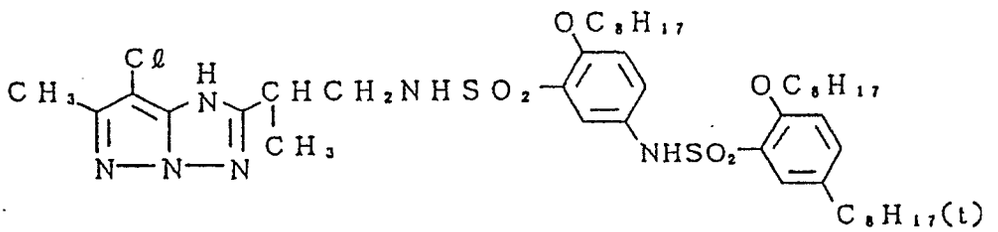

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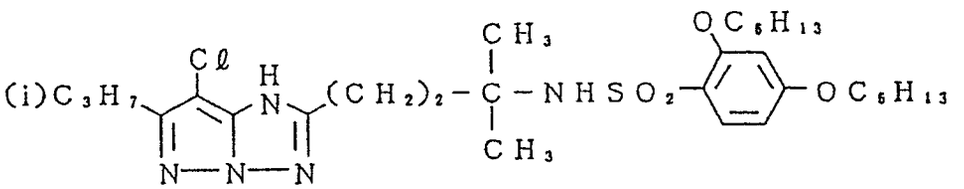

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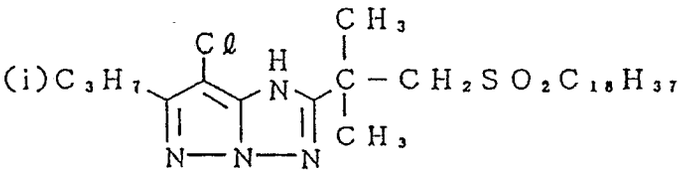

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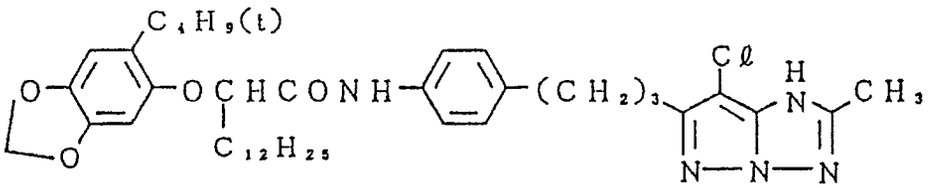

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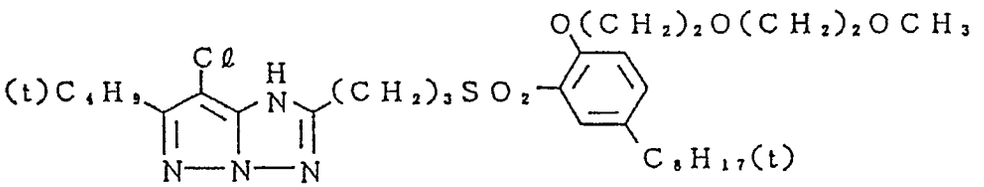

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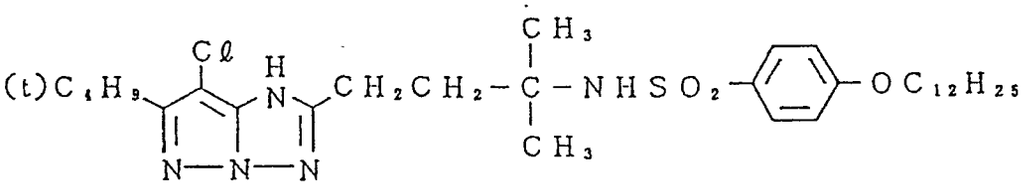

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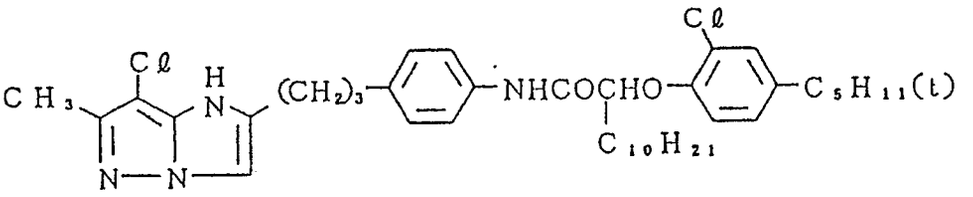

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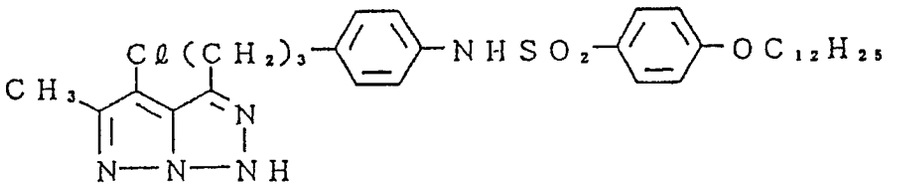

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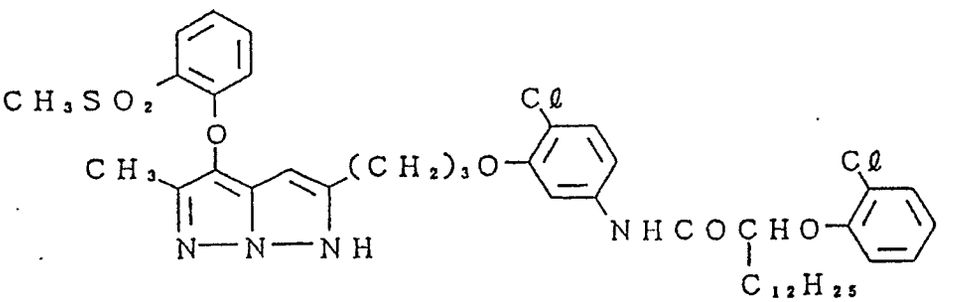

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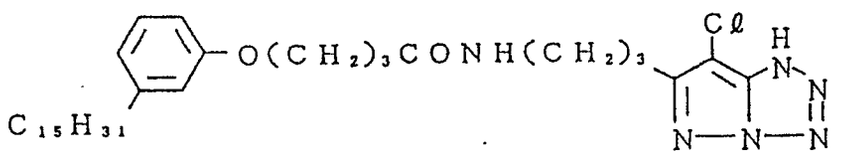

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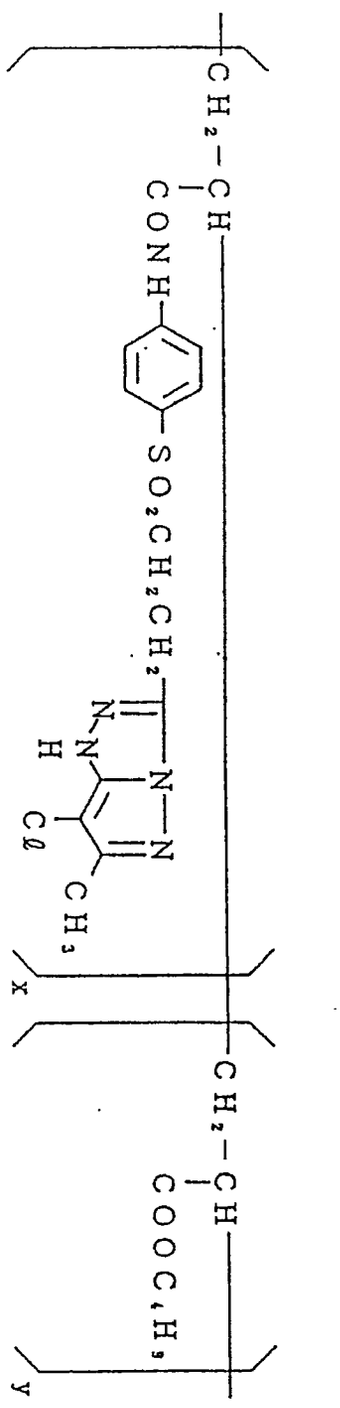
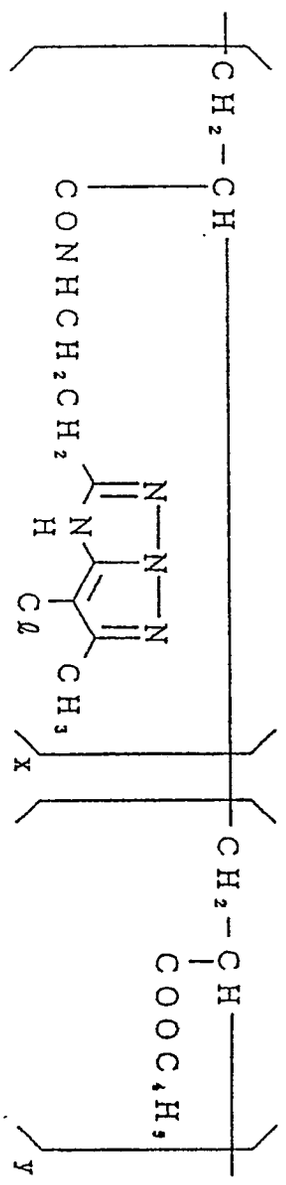


x : y = 50 : 50

M-62



x : y = 50 : 50

Besides the typical examples listed above, other magenta-dye forming couplers may be used in the present invention and they include Compound Nos. 1 - 4, 6, 8 - 17, 19 - 43, 45 - 59, 61 - 104, 106 - 121, 123 - 162, 164 -223, which are described in Unexamined Published Japanese Patent Application No. 166339/1987, page 18 upper right column to page 32, upper right column.

The couplers described hereinabove can be synthesized by making reference to Journal of the

Chemical Society, Perkin I (1977); 2047 - 2057, United States Patent 3,725,067, Unexamined Published Japanese Patent Application Nos. 99437/1984, 420045/1983, 162548/1984, 171956/1984, 33552/1985, 43659/1985, 172982/1985, 190779/1985, etc.

The magenta couplers can be used in amounts that typically range from 1×10^{-3} to 1 mole, preferably from 1×10^{-2} to 8×10^{-1} moles, per mole of silver halide.

The magenta couplers described above may be used in combination with other magenta couplers.

Phenolic or naphtholic couplers are typically used as cyan-dye forming couplers.

The photographic material of the present invention may incorporate auxiliary layers such as a filter layer, an anti-halation layer and an anti-irradiation layer. Dyes that flow out of the photographic material during development or which are bleached may be incorporated in these auxiliary layers an/or emulsion layers.

The photographic material of the present invention may also contain a matting agent, a lubricant, an image stabilizer, a formaldehyde scavenger, a uv absorber, a brightener, a surfactant, a development accelerator, a development retarder or a bleach accelerator.

The support of the photographic material may be a polyethylene-laminated paper, a polyethylene terephthalate film, a baryta paper, triacetyl cellulose, etc.

Typical examples of the scheme for processing the photographic material of the present invention are described below:

(1) color development - bleach-fixing - washing;
(2) color development - bleach-fixing - partial washing -washing;
(3) color development - bleach-fixing - washing -stabilizing;
(4) color development - bleach-fixing - stabilizing;
(5) color development - bleach-fixing - first stabilization - second stabilization;
(6) color development - washing - bleach-fixing - washing;
(7) color development - accelerated bleaching - bleach-fixing - stabilizing;
(8) color development - accelerated bleaching - bleach-fixing - washing;
(9) color development - prefixing - bleach-fixing -stabilizing;
(10) color development - pre-fixing - bleaching -stabilizing;
(11) color development - bleaching - washing -fixing -washing - stabilizing;
(12) color development - bleaching - fixing - washing -stabilizing;
(13) color development - bleaching - fixing - first stabilization - second stabilization;
(14) color development - bleaching - partial washing -fixing - partial washing - washing - stabilizing;
(15) color development - bleaching - bleach-fixing - first stabilization - second stabilization;
(16) color development - accelerated bleaching - bleaching -fixing - first stabilization - second stabilization;
(17) color development - partial washing - bleaching -partial washing - fixing - partial washing - washing -stabilizing;
(18) color development - accelerated bleaching - bleaching - partial washing - fixing - partial washing - washing - stabilizing;
(19) black-and-white development - washing (or stabilizing) - reversal - color development - bleaching - fixing -washing (optional);
(20) black-and-white development - washing (or stabilizing) - reversal - color development - accelerated bleaching - bleaching - fixing - washing (optional) -stabilizing;
(21) black-and-white development - washing (or stabilizing) - reversal - color development - bleach-fixing -washing (optional) - stabilizing; and
(22) black-and-white development - washing (or stabilizing) - reversal - color development - accelerated bleaching - bleach-fixing - fixing -washing (optional) -stabilizing.

The term "accelerated bleaching" as used hereinabove means a treatment with a pre-bath containing a bleach accelerator.

The bleaching solution or bleach-fixing solution with which the photographic material of the present invention is treated may contain any kind of bleaching agents, such as potassium ferricyanide, iron chloride (as described in British Patent No. 736,881, Japanese Patent Publication No. 44424/1981, etc.), persulfuric acid (as described in German Patent No. 2,141,199, etc.), hydrogen peroxide (as described in Japanese Patent Publication Nos. 11617/1983, 11618/1983, etc.), as well as aminopolycarboxylic acid iron (III) complex salts illustrated by ethylenediaminetetraacetic acid iron (III) complex salt. Particularly preferred examples are iron (III) complex salts of the following aminopolycarboxylic acids:

(1) ethylenediaminetetraacetic acid;
(2) diethylenetriaminepentaacetic acid;

(3) ethylenediamine-N-(β-hydroxyethyl)-N,N′, N′-triacetic acid;
(4) 1,3-diaminopropanetetraacetic acid;
(5) triethylenetetraaminehexaacetic acid;
(6) cyclohexanediaminetetraacetic acid;
(7) 1,2-diaminopropanetetraacetic acid;
(8) 1,3-diaminopropan-2-ol-tetraacetic acid;
(9) ethyl ether diaminetetraacetic acid;
(10) glycol ether diaminetetraacetic acid;
(11) ethylenediaminetetrapropionic acid;
(12) phenylenediaminetetraacetic acid;
(13) ethylenediaminetetraacetic acid disodium salt;
(14) ethylenediaminetetraacetic acid tetra (trimethylammonium) salt;
(15) ethylenediaminetetraacetic acid tetrasodium salt;
(16) diethylenetriaminepentaacetic acid pentasodium salt;
(17) ethylenediamine-N-(β-hydroxyethyl)-N,N′,N′-triacetic acid sodium salt;
(18) propylenediaminetetraacetic acid sodium salt;
(19) ethylenediaminetetramethylenephosphonic acid;
(20) cyclohexanediaminetetraacetic acid sodium salt;
(21) diethylenetriaminepentamethylenephosphonic acid;
(22) cyclohexanediaminetetramethylenephosphonic acid;
(23) nitrilotriacetic acid;
(24) iminodiacetic acid;
(25) hydroxyethyliminodiacetic acid;
(26) nitrilotripropionic acid;
(27) nitrilotrimethylenephosphonic acid;
(28) iminodimethylenephsophonic acid;
(29) hydroxyethyliminodimethylenephosphonic acid; and
(30) nitrilotriacetic acid trisodium salt.

The effectiveness of the present invention is particularly significant if iron (III) complex salts of aminopolycarboxylic acids having high molecular weights are used, and preferred aminopolycarboxylic acids are those which have molecular weights of at least 300. Among the aminopolycarboxylic acids (1) - (30) listed above, those which are particularly preferred from the viewpoint of the effectiveness of the present invention include: diethylenetriaminepentaacetic acid, 1,3-diaminopropanetetraacetic acid, 1,2-diaminopropanetetraacetic acid, 1,4-diaminobutanetetraacetic acid, glycol ether diaminetetraacetic acid and cyclohexanediaminetetraacetic acid, with diethylenetriaminepentaacetic acid and 1,3-diaminopropanetetraacetic acid being most preferred.

Iron (III) salts of aminopolycarboxylic acids are typically used in the form of free acids (hydrogen salt), alkali metal salts such as sodium salt, potassium salt and lithium salt, ammonium salts or water-soluble amine salts such as triethanolamine salt, and preferably they are used as potassium salt, sodium salt or ammonium salt. The use of at least one of these iron (III) complex salts will suffice but they may be used as admixtures. These complex salts may be used in any desired amounts, depending upon such factors as the silver content and the silver halide composition of the photographic material to be processed. Generally speaking, these complex salts have a higher oxidizing power and hence may be used at lower concentrations than other salts of aminopolycarboxylic acids. For instance, they may be used at concentrations of more than 0.01 mole per liter of processing solution, with the range of 0.05 - 0.8 moles being preferred. If these complex salts are to be used in replenishers, they are desirably concentrated to the solubility limit.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

Example 1

Preparation of samples:

Subbed cellulose acetate bases were coated, in superposition, with the layers described below, whereby Sample Nos. 11 - 39 of multi-layered color photographic material were prepared. In the following list of layers, the coating weights of silver halide and colloidal silver are indicated in grams per square

meter in terms of silver; those of additives and gelatin are indicated in grams per square meter; and those of sensitizers, couplers and DIR compounds are respectively indicated by the number of moles per mole of silver halide in the layer in which they were incorporated. The compounds of the present invention and comparative compounds used (see Table 1 below) were respectively added in an amount of 3 mmol/m^2 in the first layer (HC) in the form of either a liquid dispersion or an aqueous solution.

The emulsions incorporated in the red-, green- and blue-sensitive layers were subjected to optimum sensitization with sodium thiosulfate and chloroauric acid.

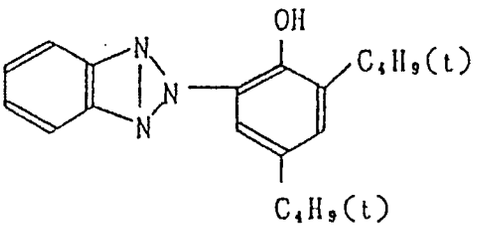
Layer	Chief ingredients	Amount
First layer (HC) (antihalation layer)	Black colloidal silver	0.20
	Gelatin	1.5
	UV absorber (UV-1)	0.1
	UV absorber (UV-2)	0.2
	Dioctyl phthalate (DOP)	0.03
	Compound of the present invention (see Table 1)	3.0
Second layer (IL-1) (intermediate layer)	Gelatin	2.0
	Anti-stain agent (AS-1)	0.1
	DOP	0.1
Third layer (R-1) (first red-sensitive emulsion layer)	AgBrI (7.5 mol% AgI), average grain size, 0.40 µm	1.2
	Gelatin	1.1
	Sensitizer I	6×10^{-4}
	Sensitizer II	1×10^{-4}
	Coupler (C-1)	0.085
	Coupler (CC-1)	0.005
	DIR compound (D-1)	0.0015
	DIR compound (D-2)	0.002
	DOP	0.6

Layer	Chief ingredients	Amount
Fourth layer (R-2) (second red-sensitive emulsion layer)	AgBrI (6.5 mol% AgI), average grain size, 0.65 μm	1.3
	Gelatin	1.1
	Sensitizer I	3×10^{-4}
	Sensitizer II	1×10^{-4}
	Coupler (C-2)	0.007
	Coupler (C-3)	0.027
	Coupler (CC-1)	0.0015
	DIR compound (D-2)	0.001
	DOP	0.2
Fifth layer (IL-2) (intermediate layer)	Gelatin	0.8
	AS-1	0.03
	DOP	0.1
Sixth layer (G-1) (first green-sensitive emulsion layer)	AgBrI (7.5 mol% AgI), average grain size, 0.40 μm	1.3
	Gelatin	1.2
	Sensitizer III	2.5×10^{-4}
	Sensitizer IV	1.2×10^{-4}
	Coupler (M-4)	0.09
	Coupler (CM-1)	0.004
	DIR compound (D-1)	0.001
	DIR compound (D-3)	0.003
	Tricresyl phosphate (TCP)	0.5

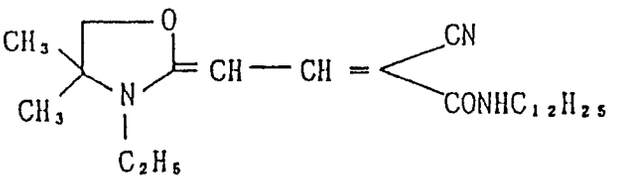
Layer	Chief ingredients	Amount
Seventh layer (G-2) (second green-sensitive layer)	AgBrI (6.5 mol% AgI), average grain size, 0.65 μm	1.4
	Gelatin	0.8
	Sensitizer III	1.5×10^{-4}
	Sensitizer IV	1.0×10^{-4}
	Coupler (M-4)	0.03
	Coupler (CM-1)	0.002
	DIR compound (D-3)	0.001
	TCP	0. 3
Eighth layer (YC) (yellow filter layer)	Gelatin	0.6
	Yellow colloidal silver	0.08
	AS-1	0.1
	DOP	0.3
Ninth layer (B-1) (first blue-sensitive emulsion layer)	AgBrI (7.5 mol% AgI), average grain size, 0.40 μm	0.5
	Gelatin	1.1
	Sensitizer V	1.3×10^{-4}
	Coupler (YB-16)	0.29
	DIR compound (D-3)	0.003
	TCP	0.2

Layer	Chief ingredients	Amount
Tenth layer (B-2) (second blue-sensitive emulsion layer)	AgBrI (6.5 mol% AgI), average grain size, 0.65 µm	0.5
	Gelatin	1.2
	Sensitizer V	1×10^{-4}
	Coupler (YB-16)	0.08
	TCP	0.1
Eleventh layer (Pro-1) (first protective layer)	Gelatin	0.55
	UV absorber (UV-1)	0.1
	UV absorber (UV-2)	0.2
	DOP	0.03
	AgBrI (1 mol% AgI), average grain size, 0.07 µm	0.5
Twelfth layer (Pro-2) (second protective layer)	Gelatin	0.5
	Polymethyl methacrylate particles (1.5 µm in dia.)	0.2
	Hardener (H-1)	0.4

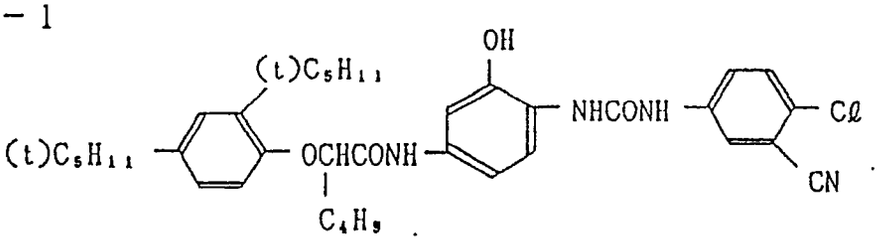
UV－1



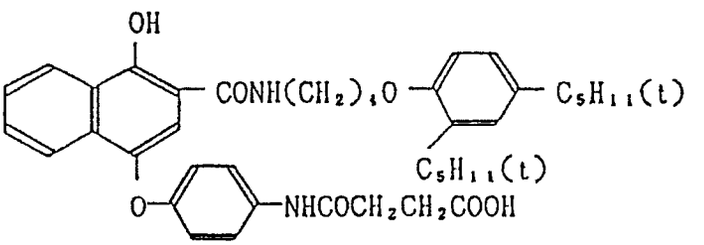
UV－2



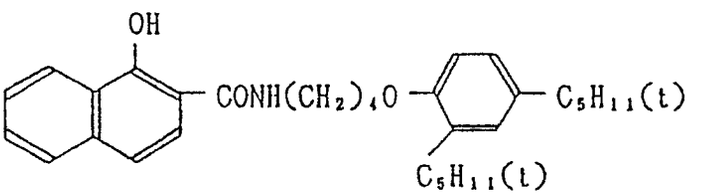
C－1



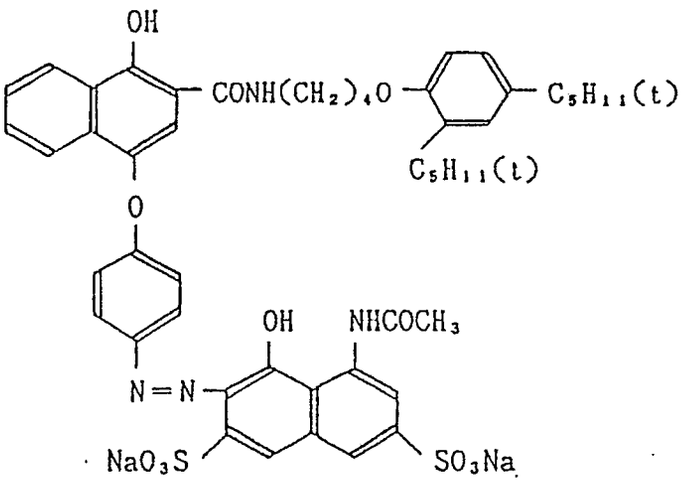
C－2



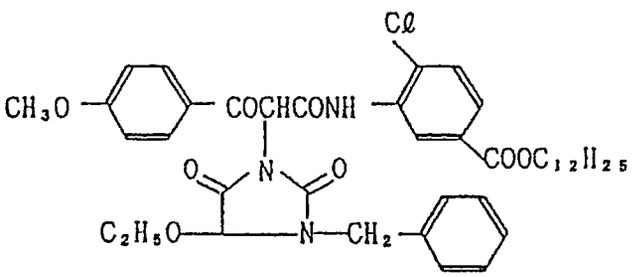
C－3



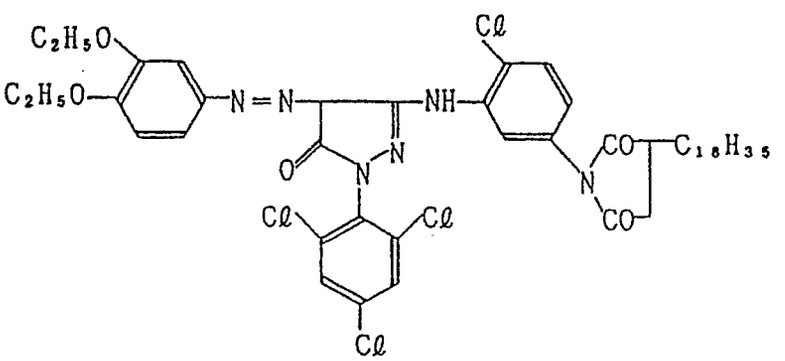
CC－1



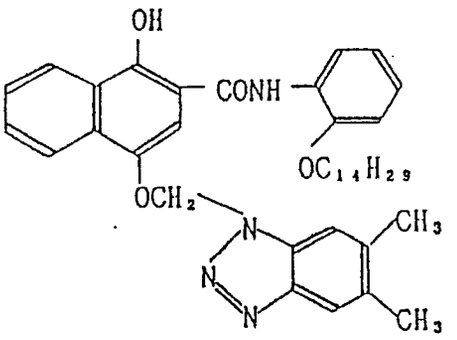
YB－16



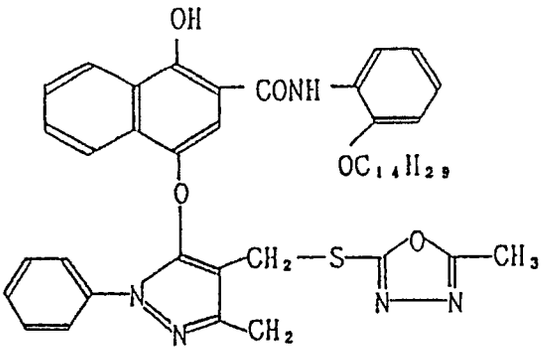
CM－1



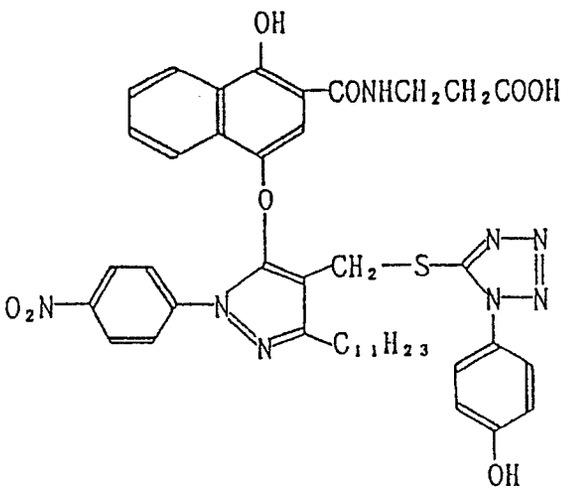
D — 1



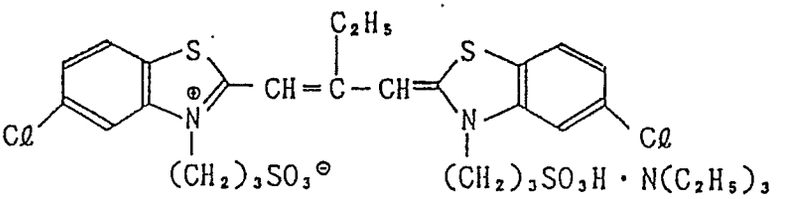
D — 2



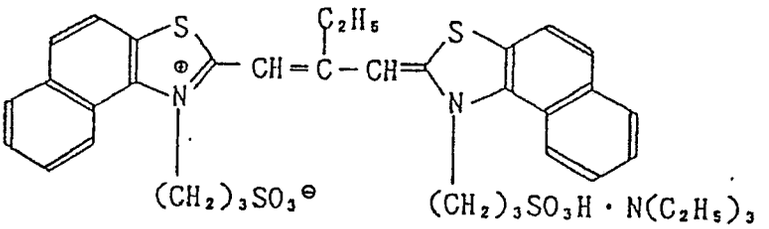
D — 3



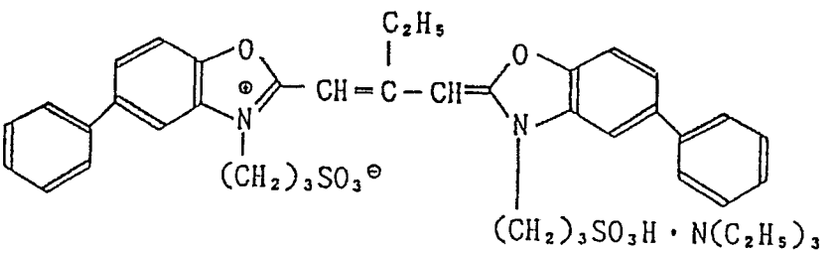
Sensitizer I



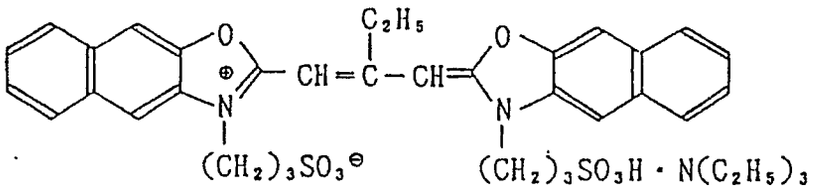
Sensitizer II



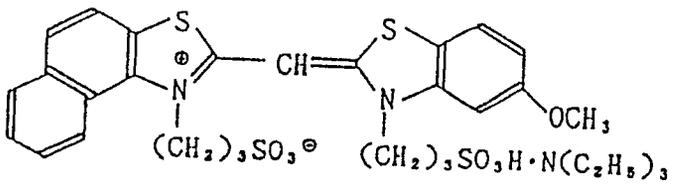
Sensitizer III



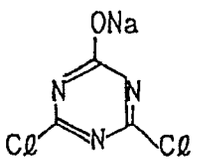
Sensitizer IV



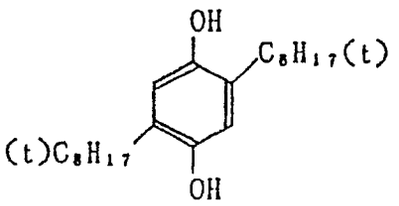
Sensitizer V



H-1



AS-1



TCP tricresyl phosphate

In the following description, the first to twelfth layers will be referred to by the respective abbreviations HC, IL-1, R-1, R-2, IL-2, G-1, G-2, YC, B-1, B-2, Pro-1 and Pro-2.

Besides the ingredients mentioned above, a surfactant was added as a coating aid to each layer.

Samples Nos. 11 - 39 were exposed through an optical wedge in the usual manner and subsequently processed by the following scheme.

Steps (38° C)	Time
Color development	3 min and 15 sec
Bleaching	See Table 1
Fixing	6 min and 30 sec
Washing	3 min and 15 sec
Stabilizing	1 min and 30 sec
Drying	

The processing solutions used had the following formulations.

Color developer	
4-Amino-3-methyl-N-ethyl-N-B-hydroxyethyl aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine hemisulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Potassium iodide	1.9 mg
Potassium bromide	1.3 g
Nitrilotriacetic acid trisodium salt (monohydroate)	2.5 g
Potassium hydroxide	1.0 g
Water	to make 1,000 ml
(pH = 10.02)	

Bleaching solution (formula A)	
Ethylenediaminetetraacetic acid iron (III) ammonium salt	100.0 g
Ethylenediaminetetraacetic acid diammonium salt	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g
Water	to make 1,000 ml
pH adjusted to 6.0 with aquous ammonia	

Bleaching solution (formula B)	
1,3-Diaminopropanetetraacetic acid iron (III) ammonium salt	180.0 g
1,3-Diaminopropanetetraacetic acid diammonium salt	4.0 g
Ammonium bromide	128.0 g
Ammonium nitrate	118.0 g
Glacial acetic acid	69.0 g
Aqueous ammonia (25%)	30 ml
Water	to make 1,000 ml
pH adjusted to 4.5 with aqueous ammonia	

Fixing solution	
Ammonium thiosulfate	175.0 g
Anhydrous ammonium sulfite	8.6 g
Sodium metasulfite	2.3 g
Water	to make 1,000 ml
pH adjusted to 6.0 with acetic acid	

Stabilizing solution	
Formaldehyde (37% aq. sol.)	1.5 ml
Konidax (Konica Corp.)	7.5 ml
Water	to make 1,000 ml

Other than said samples Nos. 11 - 39, a reference sample was also prepared in the same manner as for sample No. 11. After exposure through an optical wedge, this reference sample was processed through the sequence of color development, fixing, washing, stabilizing and drying (no bleaching was performed). The amount of residual silver in the maximum density area of the reference sample was measured with fluorescent X-rays. The amounts of residual silver in the maximum density areas of the other samples Nos. 11- 39 were measured and expressed in terms of relative values, with the value for the reference sample being taken as 100%.

The optical density for red light was measured for all samples with an optical densitometer Model PDA-65 of Konica Corp. The sensitivity was determined on the basis of the amount of exposure necessary to provide an optical density of "fog + 0.5" and expressed in terms of relative values, with the value for sample No. 11 being taken as 100.

The results are shown in Table 1.

Table 1

Sample No.		Compound	Residual silver (%)				Relative sensitivity to red light
			Bleaching solution A		Bleaching solution B		
			1 min	3 min	20 sec	40 sec	
Comparative samples	11	–	78	12	54	10	100
	12	I-2	62	13	42	11	72
	13	II-1	68	10	50	9	65
	14	III-4	70	12	54	10	72
	15	VI-12	63	11	44	10	82
	16	VII-2	52	8	33	6	62
	17	VIII-2	72	12	52	11	79
	18	XI-2	76	11	54	10	70
	19	XII-1	68	10	51	10	88
Samples of the invention	20	[I-2]·Ag	20	0	7	0	100
	21	[I-5]·Ag	34	3	13	1	99
	22	[II-1]·Ag	31	2	12	0	101
	23	[II-16]·Ag	32	3	15	1	100
	24	[III-4]·Ag	26	1	9	0	100
	25	[III-13]·Ag	24	1	10	0	99
	26	[III-24]·Ag	22	0	7	0	100
	27	[IV-1]·Ag	40	4	21	1	98
	28	[V-2]·Ag	32	3	10	0	100
	29	[VI-6]·Ag	30	2	13	0	100
	30	[VI-11]·Ag	42	4	20	1	98
	31	[VII-1]·Ag	23	0	8	0	101
	32	[VII-12]·Ag	18	0	5	0	100
	33	[VIII-2]·Ag	43	4	23	1	99
	34	[IX-5]·Ag	35	3	15	0	100
	35	[X-3]·Ag	28	0	8	0	100
	36	[XI-2]·Ag	26	1	9	0	101
	37	[XI-3]·Ag	32	2	13	0	100
	38	[XII-1]·Ag	30	0	9	0	100
	39	[XII-5]·Ag	35	3	14	0	99

As is clear from Table 1, samples Nos. 20 - 39 containing the compounds of the present invention showed good desilvering quality without experiencing a decrease in sensitivity, but sample Nos. 12 - 19 containing compounds that did not form silver salts experienced substantial loss in sensitivity and hence did not have good photographic performance.

Example 2

Sample Nos. 11 - 39 prepared in Example 1 were exposed through an optical wedge in the usual manner and subsequently processed by the following scheme.

Steps (38° C)	Time
Color development	3 min and 15 sec
Bleach-fixing	See table 2
Washing	3 min and 15 sec
Stabilizing	1 min and 30 sec
Drying	

The processing solutions used had the following formulations.

Color developer

Same as in Example 1.

Bleach-fixing solution	
Ethylenediaminetetraacetic acid iron (III) ammonium salt	60.0 g
Ethylenediaminetetraacetic acid ammonium salt	3.0 g
Ammonium thiosulfate (70% aq. sol.)	130.0 ml
Ammonium sulfite (40% aq. sol.)	27.5 ml
Color developer (see above)	100.0 ml
Water	to make 1,000 ml
pH adjusted to 7.0 with potassium carbonate or glacial acetic acid.	

Stabilizing solution

Same as in Example 1.

The relative amount of residual silver was determined for each sample as in Example 1. The results are shown in Table 2.

Table 2

Sample No.		Residual silver (%)	
		Time of bleach-fixing	
		1 min and 30 sec	3 min and 15 sec
Comparative samples	11	63	21
	12	48	11
	13	57	19
	14	60	19
	15	55	13
	16	42	9
	17	58	18
	18	60	20
	19	53	13
Samples of the invention	20	6	0
	21	15	2
	22	11	1
	23	12	1
	24	8	1
	25	6	0
	26	8	0
	27	30	3
	28	24	2
	29	22	0
	30	29	3
	31	6	0
	32	4	0
	33	29	3
	34	23	2
	35	19	1
	36	15	0
	37	20	2
	38	18	0
	39	25	2

As is clear from Table 2, sample Nos. 20 - 39 containing the compounds of the present invention showed much better desilvering quality than the comparative samples in the bleach-fixing treatment.

Example 3

Samples of color photographic material were prepared using I-6, I-9, II-10, II-23, III-6, III-11, III-14, V-1, VI-2, VI-17, VII-6, VII-10, VIII-1, VIII-6, IX-3, X-4, X-6, XI-5, XI-6, XII-2 and XII-7 as compounds (B) to form compounds (B)•Ag of the present invention. When these samples were subjected to experiments under completely identical conditions to Examples 1 and 2, the effectiveness of the present invention was verified.

Example 4

Additional sample Nos. 41 - 47 were prepared by modifying sample No. 32 of Example 1 in such a way that the magenta-dye forming coupler in layers G-1 and G-2 was changed to those shown in Table 3. These

samples were subjected to experiments under the same conditions as in Example 1. The results are shown in Table 3 together with the data for sample No. 32.

Table 3

Sample No.		Magenta coupler	Residual silver (%)				Relative sensitivity to red light
			Bleaching solution A		Bleaching solution B		
			1 min	3 min	20 sec	40 sec	
Samples of the invention	32	M-4	18	0	5	0	100
	41	M-1	20	0	5	0	100
	42	M-2	17	0	4	0	101
	43	M-19	18	0	5	0	99
	44	M-25	18	0	5	0	100
	45	M-34	20	0	6	0	100
	46	M-51	17	0	5	0	99
	47	M-56	19	0	5	0	101

Table 3 shows that the samples of the present invention achieved satisfactory results in terms of both desilvering quality and sensitivity irrespective of the type of magenta-dye forming coupler used.

Example 5

Additional sample Nos. 51 - 56 were prepared by modifying sample No. 32 of Example 1 in such a way that the yellow-dye forming coupler in layers B-1 and B-2 was changed to those shown in Table 4. These samples were subjected to experiments under the same conditions as in Example 1. The results are shown in Table 4 together with the data for sample No. 32.

Table 4

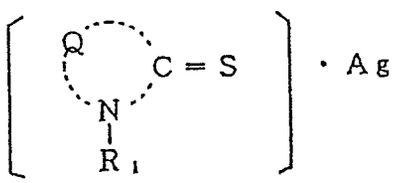
Sample No.		Yellow coupler	Residual silver (%)				Relative sensitivity to red light
			Bleaching solution A		Bleaching solution B		
			1 min	3 min	20 sec	40 sec	
Samples of the invention	32	YB-16	18	0	5	0	100
	51	YB-21	18	0	5	0	100
	52	YB-15	17	0	5	0	101
	53	YB-17	18	0	5	0	100
	54	YB-18	19	0	6	0	99
	55	YB-19	18	0	5	0	100
	56	YB-20	19	0	5	0	100

Table 4 shows that the samples of the present invention achieved satisfactory results in terms of both desilvering quality and sensitivity irrespective of the type of yellow-dye forming coupler used.

As will be understood from the foregoing description, the present invention provides a silver halide color photographic material that has such a good desilvering quality that it can be desilvered in a shorter time than has been necessary in the prior art.

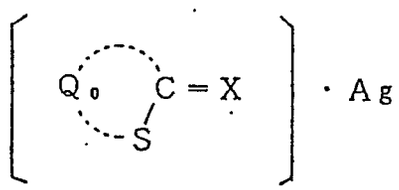
Claims

1. A silver halide color photographic material comprising a support, a light-sensitive silver halide emulsion layer and a non-light-sensitive layer, said material containing at least one of the compounds represented by the following general formulas (I) - (XII):



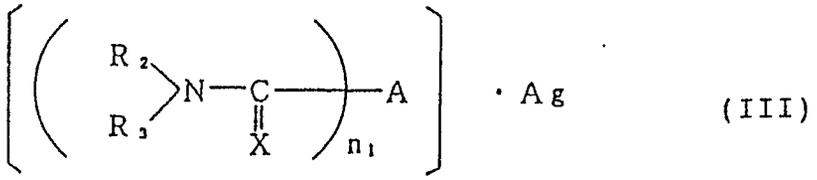
(I)

where Q is the atomic group necessary to form the nitrogenous hetero ring; R_1 is an alkyl group, a cycloalkyl group, an aryl group, a hetero ring or an amino group;



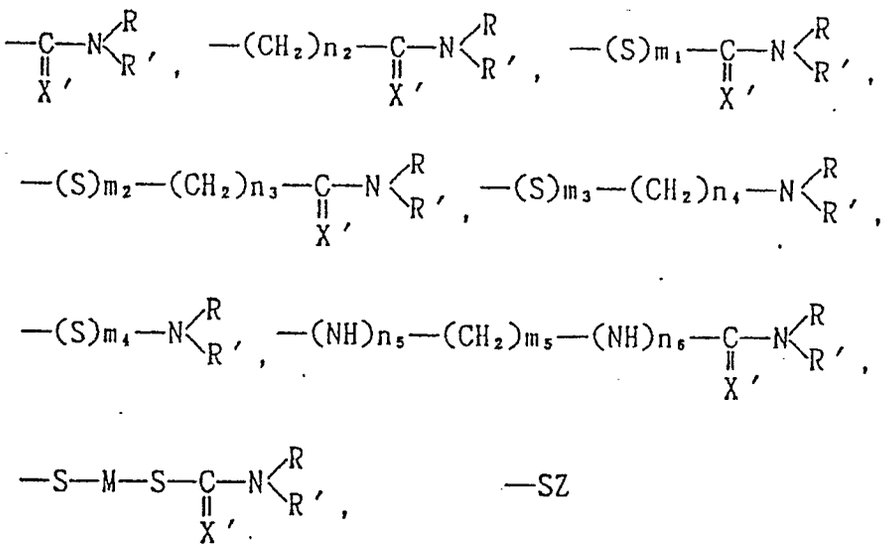
(II)

where Qo is the atomic group necessary to form the sulfureous hetero ring; X is O, S or NR (R is a hydrogen atom or an alkyl group);

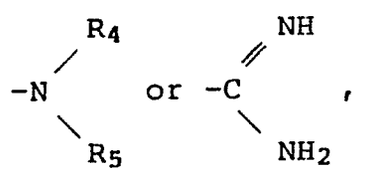


(III)

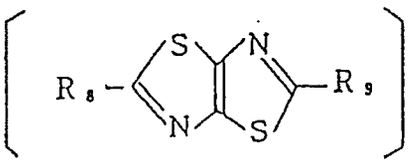
where R_2 and R_3 are each independently a hydrogen atom, an alkyl group, a hydroxyl group, a carboxyl group, an amino group, an acyl group, an aryl group or an alkenyl group; A is



or an n_1-valent heterocyclic residue; X is =S, =O or =NR″ (where R and R′ respectively have the same meanings as R_2 and R_3; X′ has the same meaning as X; Z is an ammonium group, an amino group, a nitrogenous heterocyclic residue, an alkyl group or -B-Y; M is a divalent group of metallic atoms; R″ is a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic residue or an amino group; n_1 - n_6 and m_1 - m_4 are each an integer of 1 - 6; m_5 is an integer of 0 - 6; B is an alkylene group; Y is

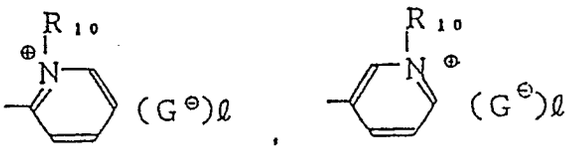


where R_4 and R_5 respectively have the same meanings as R_2 and R_3, provided that R_2 and R_3, R and R′ and R_4 and R_5 may respectively combine to form a ring;

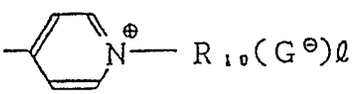


(IV)

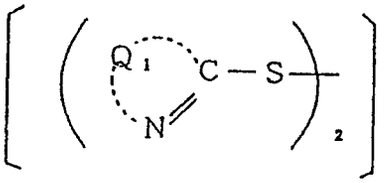
where R_8 and R_9 are each



or

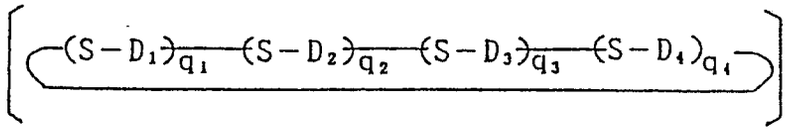


R_{10} is an alkyl group or $-(CH_2)_{n8}SO_3\ominus$ (provided that when R_{10} is $-(CH_2)_{n8}SO_3\ominus$, ℓ is O, and when R_{10} is an alkyl group, ℓ is 1); G⊖ is an anion; and n_8 is an integer of 1 - 6;



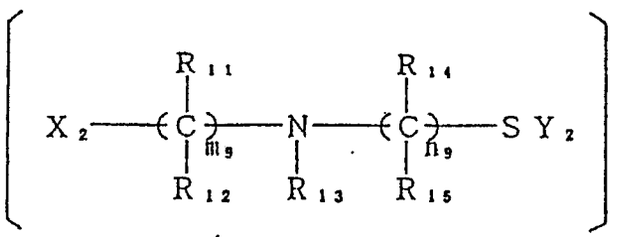
(V)

where Q_1 is the atomic group necessary to form the nitrogenous hetero ring;



(VI)

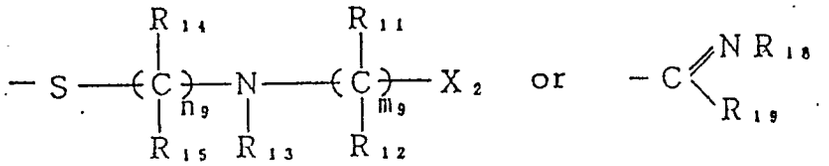
where D_1, D_2, D_3 and D_4 are each a simple bond or a hydrocarbon chain; q_1, q_2, q_3 and q_4 are each 0, 1 or 2;



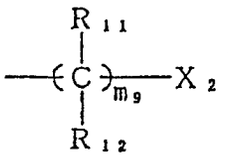
(VII)

where X_2 is a hydrogen atom, R_{16}, -COOM′, -OH, $-SO_3M'$ $-CONH_2$, $-SO_2NH_2$, $-NH_2$, -CN, $-CO_2R_{16}$, $-SO_2R_{16}$, $-OR_{16}$, $-NR_{16}R_{17}$, $-SR_{16}$, $-SO_3R_{16}$, $-NHCOR_{16}$, $-NHSO_2R_{16}$, $-OCOR_{16}$ or $-SO_2R_{16}$;

Y_2 is

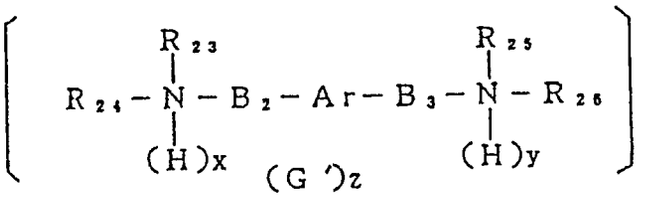


m_9 and n_9 are each an integer of 1 - 10; R_{11}, R_{12}, R_{14}, R_{15}, R_{17} and R_{18} are each a hydrogen atom, an alkyl group or an acyl group; R_{13} is a hydrogen atom, an alkyl group, an acyl group or



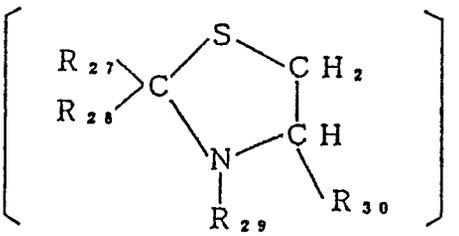
;

R_{16} is an alkyl group; R_{19} is $-NR_{20}R_{21}$, $-OR_{22}$ or $-SR_{22}$; R_{20} and R_{21} are each a hydrogen atom or an alkyl group; R_{22} is the atomic group necessary to form a ring in combination with R_{18}; R_{20} or R_{21} may combine with R_{18} to form a ring; and M′ is a hydrogen atom or a cation;



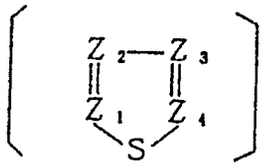
(VIII)

where Ar is an arylene or a divalent organic group containing an arylene group; B_2 and B_3 are each an alkylene group; R_{23}, R_{24}, R_{25} and R_{26} are each a hydroxy-substituted alkyl group; x and y are each 0 or 1; G′ is an anion; and z is 0, 1 or 2;



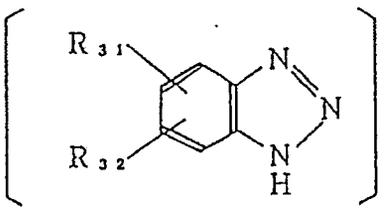
(IX)

where R_{27} and R_{28} are each a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; R_{29} is a hydrogen atom or an alkyl group; R_{30} is a hydrogen atom or a carboxyl group;



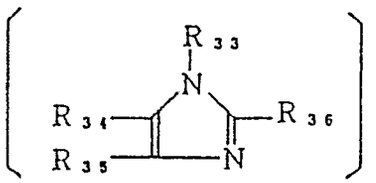
(X)

where Z_1, Z_2, Z_3 and Z_4 are each a carbon atom or a nitrogen atom, and at least one of these is a nitrogen atom;



(XI)

where R_{31} and R_{32} are each a hydrogen atom or substituent; and



(XII)

where R_{33}, R_{34}, R_{35} and R_{36} are each a hydrogen atom or a substituent.

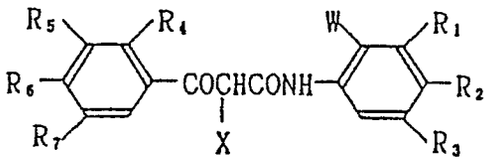
2. A silver halide color photographic material according to claim 1 wherein said non-light-sensitive layer contains at least one of the compounds of the general formulas (I) -(XII).

3. A silver halide color photographic material according to claim 2 wherein said non-light-sensitive layer lies between the support and the light-sensitive silver halide emulsion layer situated closest to the support.

4. A silver halide color photographic material according to claim 1 wherein one or more of the compounds of the general formulas (I) - (XII) are contained in a total amount of 1×10^{-4} - 100 g per square meter of the photographic material.

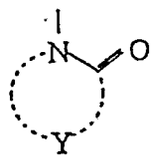
5. A silver halide color photographic material according to claim 4 wherein one or more of the compounds of the general formulas (I) - (XII) are contained in a total amount of 1×10^{-2} - 1 g per square meter of the photographic material.

6. A silver halide color photographic material according to claim 1 which contains a yellow-dye forming coupler represented by the following general formula (YB-I):



(YB-I)

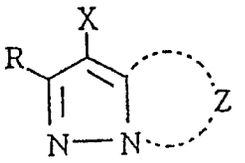
where R_1 - R_7 and W are each a hydrogen atom or a substituent; preferably, R_1, R_2 and R_3, which may be the same or different, each represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alkoxy group, an acylamino group, a carbamoyl group, an alkoxycarbonyl group, a sulfonamido group or a sulfamoyl group; R_4, R_5, R_6 and R_7, which may be the same or different, each preferably represents a hydrogen atom, an alkyl group, an alkoxy group, an aryloxy group, an acylamino group or a sulfonamide group; W is preferably a halogen atom, an alkyl group, an alkoxy group, an aryloxy group or a dialkylamino group; X is a hydrogen atom or a group that can be eliminated, and a preferred group that can be eliminated is represented by the following general formula (YB-II):



(YB-II)

where Y is a group of the non-metallic atoms necessary to form a 5- or 6-membered ring.

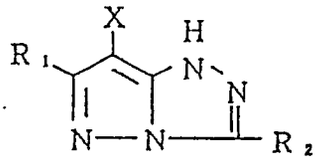
7. A silver halide color photographic material according to claim 1 which contains a magenta-dye forming coupler represented by the following general formula (M-I):



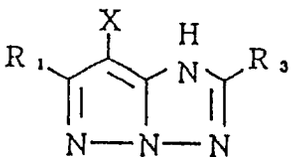
(M-I)

where Z is a group of the non-metallic atoms necessary to form the nitrogenous heterocyclic ring which may contain a substituent; X is a hydrogen atom or a group capable of leaving upon reaction with the oxidation product of a color developing agent; and R is a hydrogen atom or a substituent.

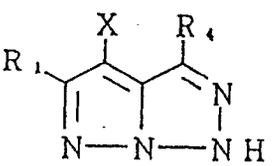
8. A silver halide color photographic material according to claim 7 wherein the magenta-dye forming coupler represented by the general formula (M-I) is represented more specifically by either one of the following general formulas (M-II) to (M-VII):



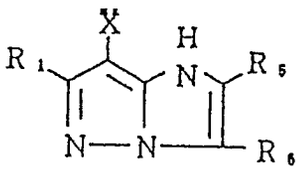
(M-II)



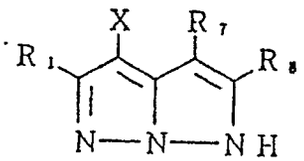
(M-III)



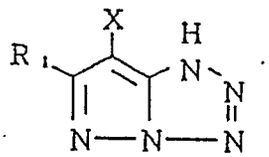
(M-IV)



(M-V)



(M-VI)



(M-VII)

where R_1 - R_8 and X respectively have the same meanings as R and X already defined.

9. A method of processing the silver halide color photographic material recited in claim 1, which includes the step of performing bleaching in the presence of an iron (III) complex salt of aminopolycarboxylic acid.

10. A method according to claim 9 wherein said aminopolycarboxylic acid has a molecular weight of at least 300.

11. A method according to claim 9 wherein said iron (III) complex salt of aminopolycarboxylic acid is used in an amount of at least 0.01 mole per liter of the processing solution used.

12. A method according to claim 9 wherein said iron (III) complex salt of aminopolycarboxylic acid is used in an amount of 0.05 - 0.8 moles per liter of the processing solution used.

13. A silver halide color photographic material containing a compound of the formula (B).Ag where B represents a nitrogen-and/or sulfur-containing compound which can be cyclic.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 7384

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 163 669 (E.KANADA ET AL.) * column 3, line 51 - column 7, line 31; claims *	1-13	G 03 C 7/392
A	EP-A-0 234 742 (KONISHIROKU PHOTO INDUSTRY) * claims *	6-12	
A	EP-A-0 317 951 (EASTMAN KODAK) * claims *		
A	DE-A-3 227 962 (AGFA-GEVAERT) * pages 9 - 10; claims *		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	23 October 90	PHILOSOPH L.P.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
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&: member of the same patent family, corresponding document