⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 301 477**
A2

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: **88112038.0**

㉒ Date of filing: **26.07.88**

(51) Int. Cl.4: **G03C 7/32 , G03C 7/34 ,**
//C07C149/437

㉚ Priority: **27.07.87 JP 186939/87**

(43) Date of publication of application:
01.02.89 Bulletin 89/05

(84) Designated Contracting States:
DE FR GB NL

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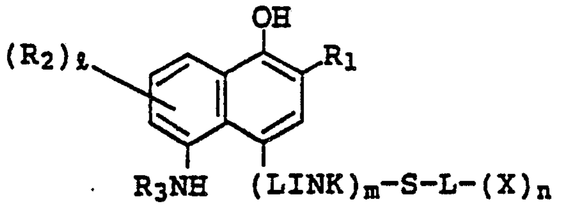
(54) Silver halide color photosensitive material and method of processing thereof.

(57) A silver halide color photosensitive material comprising at least one silver halide emulsion layer on a support, which contains at least one bleaching accelerator releasing type coupler represented by the following Formula (I):



(I)

The coupler according to the present invention can provide sufficient and stable cyan images when processed in a bleach-fix bath at low pH which is effective to the improvement of the silver-removing rate.

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SILVER HALIDE COLOR PHOTOSENSITIVE MATERIAL AND METHOD OF PROCESSING THEREOF

FIELD OF THE INVENTION

The present invention concerns a silver halide color photosensitive material.

BACKGROUND OF THE INVENTION

Silver halide color photosensitive material is generally processed fundamentally in a color developing step and a desilvering step. In the color developing step, exposed silver halide is reduced by a color developing agent to produce silver, while the oxidized color developing agent reacts with a coupler to provide a dyed image. The thus formed silver is oxidized with a bleaching agent in the succeeding desilvering step and further undergoes the effect of a fixing agent into a soluble silver complex which is then removed by dissolution.

In recent years, more rapid processing (i.e., shortening for the time required for the processing) is strongly demanded in the relevant field of the art and, particularly, shortening of the desilvering step which occupies nearly one-half of the processing time. However, shortening the desilvering step causes remarkable problems.

As a method of increasing the bleaching power, Research Disclosure Item Nos. 24241 and 11449 and JP-A-61-201247 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") describe couplers of bleach accelerating compound releasing type, and it has been known that the desilvering performance can be improved by using a silver halide color photosensitive material containing such a coupler of bleach accelerating compound releasing type.

However, if photosensitive material containing the coupler of bleach accelerating compound releasing type is used for the rapid processing in the desilvering step therefor, it has been found that the color reproducibility of a cyan image is worsened remarkably.

On the other hand, various cyan image-forming couplers effective to the improvement for the reproducibility of cyan image have been known (for example, U.S. Patent 4,333,999, JP-A-57-207593, JP-A-57-2045448, JP-A-58-11863, etc. describe phenol type cyan couplers having a ureido group at the 2 position, JP-A-60-237448, JP-A-61-145557 and JP-A-61-153640 describe a naphthol type cyan coupler having amido group at the 5-position and, further, 2,5-diacylamino substituted phenol type cyan coupler known in the field of the color paper, etc.). Also, in JP-A-61-201247 concerning a coupler of the bleach accelerating compound releasing type described above, a phenol type cyan coupler having a 4-cyanophenylureido group at the 2-position is used as a kind of the cyan image-forming coupler effective to such a reproducibility. .

In addition, it has been known that the situation is the same for the dark place storability of a cyan image. That is, dark heat fastness of a cyan color image can remarkably be improved by using a phenol type cyan coupler having a ureido group at the 2-position, a 2,5-diacylamino substituted phenol type cyan coupler, or a naphthol type cyan coupler having an amido group at the 5-position.

However, all of the cyan couplers releasing desilverization accelerator known at present have a serious drawback that they are poor in the color reproducibility and dark heat fastness. Furthermore, it has been found that if means for increasing the desilvering rate more (for example, lowering the pH value of a bleach fix bath etc.), is used, worsening of the color reproducibility described above becomes remarkable for the existent desilvering accelerator releasing coupler.

Such disadvantages aggravate the problem of making the desilvering step easier and faster.

Although the coupler having a 2-ureido substituted phenol nuclei as described in JP-A-61-201247 can compensate the foregoing drawbacks, it results in additional drawbacks such as increased color residue of sensitizing dye upon applying high speed processing or low replenishing processing, or poor coupling activity of the coupler.

SUMMARY OF THE INVENTION

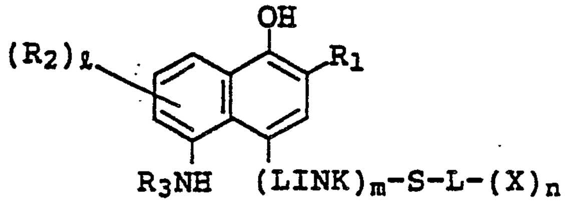
The present invention has been achieved with an aim of overcoming such additional problems described above in a silver halide color photosensitive material containing a bleaching accelerator releasing coupler.

Accordingly, it is a first object of the present invention to provide a silver halide color photographic material excellent in speeding up the desilvering step and having satisfactory color reproducibility or image storability.

The second object of the present invention is to provide a novel desilvering accelerator releasing coupler having excellent coupling activity and not causing increase in the minimum image density. This novel coupler should also increase the processing speed, decrease replenisher, and save water washing for the processing.

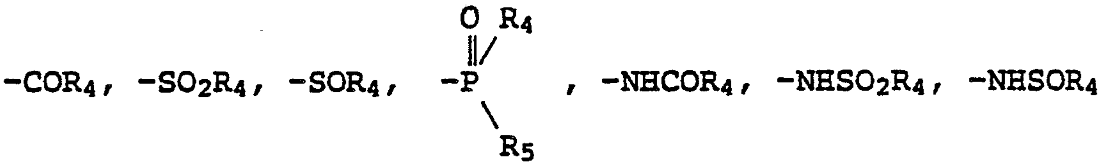
The foregoing objects of the present invention can be attained by providing:

(1) a silver halide color photosensitive material comprising at least one silver halide emulsion layer on a support, which contains at least one bleaching accelerator releasing type coupler represented by the following Formula (I):

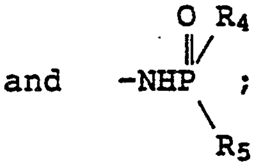


(I)

wherein R_1 is selected from the group consisting of a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an amidino group, a guanidino group,



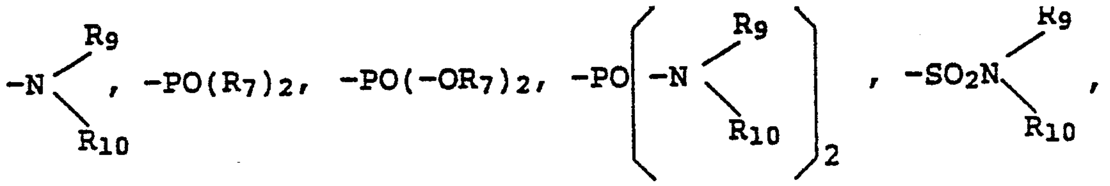
$$-COR_4,\ -SO_2R_4,\ -SOR_4,\ -\mathrm{P}(=\mathrm{O})(R_4)R_5,\ -NHCOR_4,\ -NHSO_2R_4,\ -NHSOR_4$$



$$\text{and}\quad -NH\mathrm{P}(=\mathrm{O})(R_4)R_5\ ;$$

R_2 represents a halogen atom, a hydroxyl group, a carboxyl group, a sulfo group, an amino group, a cyano group, a nitro group, an aliphatic group, an aromatic group, a carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a ureido group, an acyl group, an acyloxy group, an aliphatic oxy group, an aromatic oxy group, an aliphatic thio group, an aromatic thio group, an aliphatic sulfonyl group, an aromatic sulfonyl group, an aliphatic sulfinyl, an aromatic sulfinyl group, an aliphatic oxy carbonyl group, an aromatic oxy carbonyl group, an aliphatic oxycarbonylamino group, an aromatic oxy carbonylamino group, a sulfamoyl amino group, a heterocyclic group and an imido group; ℓ represents an integer of 0 to 3; R_3 is selected from the group consisting of a hydrogen atom and R_6Y; LINK represents a functional linkage group connecting by way of a hetero atom to the 4-position of a naphthol ring; m represents 0 or 1; L is selected from the group consisting of a (n+1) valent group, that is, an alkyl group with 1 to 8 carbon atoms, an aromatic group with 6 to 10 carbon atoms, and a heterocyclic group with 1 to 10 carbon atoms each removed with hydrogen atoms by the number of n; X represents a water soluble substituent; n represents an integer 1 to 3, provided that:

R_4 and R_5 represent independently an aliphatic group, an aromatic group, a heterocyclic group, an amino group, an aliphatic oxy group or an aromatic oxy group, R_6 represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, $-OR_7$, $-SR_7$, $-COR_8$,



$$-N{<}^{R_9}_{R_{10}},\ -PO(R_7)_2,\ -PO(-OR_7)_2,\ -PO\left(-N{<}^{R_9}_{R_{10}}\right)_2,\ -SO_2N{<}^{R_9}_{R_{10}},$$

$-CO_2R_7$, $-SO_2R_7$, $-SO_2OR_7$ and an imido group; Y is selected from the group consisting of $>N-R_9$, -CO-, $-SO_2-$, -SO- and a single bond. R_7 is selected from the group consisting of an aliphatic group, an aromatic group and a heterocyclic group; R_8 is selected from the group consisting of a hydrogen atom, an aliphatic group, an aromatic group and a heterocyclic group; R_9 and R_{10} are both selected independently from the group consisting of a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an aliphatic sulfonyl group and an aromatic sulfonyl group.

In a case where ℓ is 2 or greater, each R_2 may be identical to or different from the other(s), or an R_2 may join with another R_2 to form a ring. Further, an R_2 may form a dimer or higher polymeric form (oligomer or polymer) which is bonded by way of a divalent or higher valent group in any of R_1, R_2, or R_3.

(2) A method of processing a silver halide color photosensitive material wherein a silver halide color photosensitive material comprising at least one silver halide emulsion layer on a support and containing at least one bleach accelerator releasing type coupler represented by Formula (I) is processed in a bleach-fix bath without water washing after color development.

(3) A method of processing a silver halide color photosensitive material as defined in (2) above wherein the pH value of the bleach-fix bath is 5.7 or less.

(4) A method of processing a silver halide color photosensitive material, wherein the method comprises a step of applying water washing or stabilization directly after the fixing or bleach-fix processing to the silver halide color photosensitive material, which material has at least one silver halide emulsion layer on a support and contains at least one bleach accelerator releasing type coupler represented by Formula (I); the water washing or the stabilization step includes a plurality of vessels and, upon replenishing a processing solution in a multistage countercurrent system, the replenishing amount is from 0.1 to 50 times of the amount of the processing solution carried from the preceeding bath per unit area of the silver halide color photosensitive material to be processed.

DETAILED DESCRIPTION OF THE INVENTION

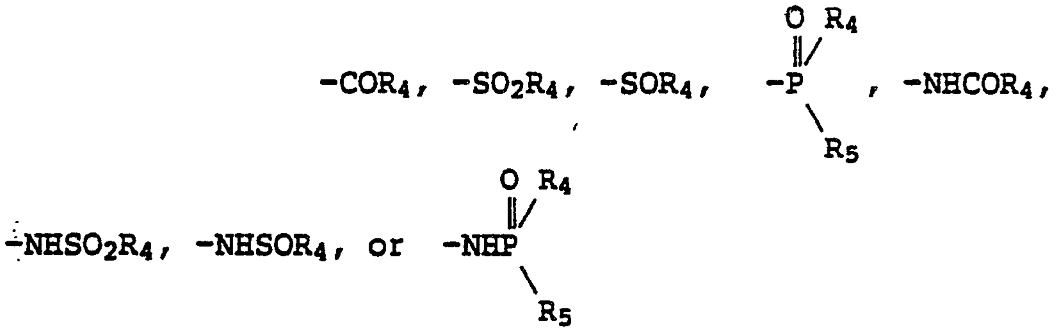
Any aliphatic group used in the compounds of the present invention may be linear, branched or cyclic alkyl groups, alkenyl groups or alkynyl groups which may be substituted or unsubstituted. Aromatic group of the present invention may be substituted or unsubstituted aryl groups including a condensed ring. Heterocyclic rings may be a substituted or unsubstituted, single or condensed heterocyclic ring. Specific examples of the aliphatic groups suitable for the present invention can include methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, cyclopentyl, t-pentyl, cyclohexyl, n-octyl, 2-ethylhexyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, 2-hexyldecyl, adamantly, trifluoromethyl, carboxymethyl, methoxyethyl, vinyl, allyl, hydroxyethyl, heptafluoropropyl, benzyl, phenetyl, phenoxyethyl, methylsulfonylethyl, methane sulfonamide ethyl, 3-(2-ethylhexyloxy)propyl, 3-n-decyloxypropyl, 3-n-dodecyloxypropyl, 3-n-tetradecyloxypropyl, oleyl, propalgyl, ethynyl, 3-(2,4-di-t-pentylphenoxy)propyl, 4-(-2,4-di-t- pentylphenoxy)-butyl, 1-(2,4 di-t-pentylphenoxy)propyl, 1-(2,4-di-t-pentylphenoxy)pentyl, 1-(3-tetradecyl phenoxy)propyl and 2-n-dodecylthioethyl.

Specific examples of aromatic groups suitable for the present invention can include phenyl, p-tolyl, m-tolyl, o-tolyl, 4-chlorophenyl, 4 nitrophenyl, 4-cyanophenyl, 4-hydroxyphenyl, 3-hydroxyphenyl, 1-naphthyl, 2-naphthyl, o-biphenyl, p-biphenyl, pentafluorophenyl, 2-methoxyphenyl, 2-ethoxyphenyl, 4-methoxyphenyl, 4-t-butylphenyl, 4-t-octylphenyl, 4-carboxyphenyl, 4-methane sulfoneamidephenyl, 4-(4-hydroxyphenylsulfonyl)phenyl, 2-n-tetradecyloxyphenyl, 4-n-tetradecyloxyphenyl, 2-chloro-5-n-dodecyloxyphenyl, 3-n-pentadecylphenyl, 2-chlorophenyl, 4-methoxycarbonylphenyl, 4 methylsulfonylphenyl, and 2,4-di-t-pentylphenyl.

Specific examples of the heterocyclic ring suitable for the present invention can include 2-pyridyl, 3-piridyl, 4-piridyl, 2-furyl, 2-thienyl, 3-thienyl, 4-quinolyl, 2-imidazolyl, 2-benzimidazolyl, 4-pyrazolyl, 2-benzoxazolyl, 2-benzothiazolyl, 1-imidazolyl, 1-pyrazolyl, 5-tetrazolyl, 1,3,4-thiadiazol-2-yl, 2-prolyl, 3-triazolyl, 4-oxazolyl, 4-thiazolyl, 2-pyrimidyl, 1,3,5-triazine-2-yl, 1,3,4-oxadiazol-2-yl, 5-pyrazolyl, 4-pyrimidyl, 2-pyrazyl, succinimido, phthal imido, morpholino, pyrroridino, piperidino, imidazolidine-2,4-di-ole-3-yl, imidazolidine 2,4 dion-1-yl, and oxazolyzine 2,4-dion-3-yl.

Individual substituents in Formula (I) are to be described specifically next.

In Formula (I) R_1 represents a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an amidino group, a guanidino group or the group represented by



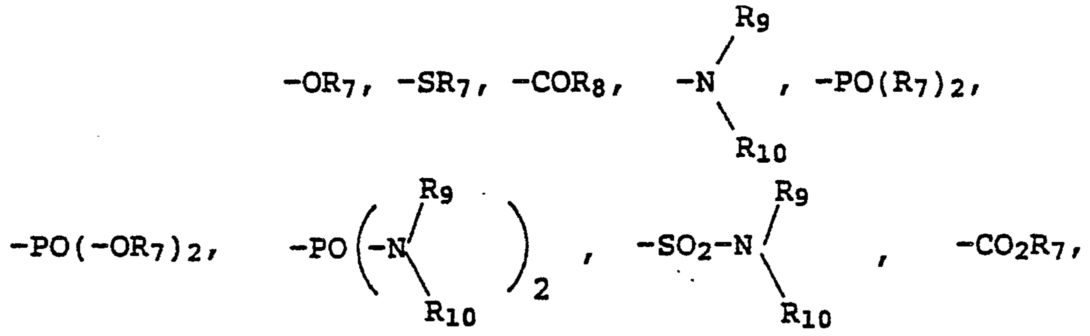
$$-COR_4,\ -SO_2R_4,\ -SOR_4,\ -\overset{O}{\overset{\|}{P}}(R_4)(R_5),\ -NHCOR_4,$$

$$-NHSO_2R_4,\ -NHSOR_4,\ \text{or}\ -NH\overset{O}{\overset{\|}{P}}(R_4)(R_5)$$

wherein R_4 and R_5 each representsan aliphatic group with 1 to 30 carbon atoms, an aromatic group with 6 to 30 carbon atoms, a heterocyclic group with 1 to 30 carbon atoms, an amino group with 0 to 30 carbon atoms (for example, amino, methylamino, dimethylamino, n-butylamino, anilino, N-(2-n-tetradecyloxyphenyl)amino, pyrolidino, morpholino, piperidino, 2-ethylhexylamino, n-dodecylamino, N-methyl-N-dodecylamino, 3 dodecyloxypropylamino, 3-(2,4-di-t-pentylphenoxy)propylamino, 4-(2,4-di-t-pentylphenoxy)-butylamino); an aliphatic oxy group with 1 to 30 carbon atoms (for example, methoxy, ethoxy, buthoxy, methoxyethoxy, n-dodecyloxy, 3-(2,4-di-t- pentylphenoxy)propoxy); or an aromatic oxy group with 6 to 30 carbon atoms (for example, phenoxy, 4-n-dodecyloxyphenoxy, 4-methoxycarbonylphenoxy). R_4 and R_5 may join with each other to form a ring. If R_1 represents a halogen atom, the halogen atom can include e.g., fluorine atom, chlorine atom, bromine atom or iodine atom. If R_1 represents an amidino group or guanidino group, the number of carbon atoms thereof is from 1 to 30 which may be substituted with an aliphatic group, an aromatic group, a hydroxyl group, an aliphatic oxy group, an acyl group, an aliphatic sulfonyl group, an aromatic sulfonyl group, an acyloxy group, an aliphatic sulfonyloxy group or an aromatic sulfonyloxy group, or two nitrogen atoms may join with each other to form a heterocyclic ring such as imidazole or benzimidazole.

In Formula (I), R_2 represents a halogen atom, (for example, fluorine, chlorine, bromine or iodine), a hydroxyl group, a carboxyl group, a sulfo group, a cyano group, a nitro group, an amino group with 0 to 30 carbon atoms (for example, amino, methylamino, dimethylamino, pyrrolidino, anilino), an aliphatic group with 1 to 30 carbon atoms, an aromatic group with 6 to 30 carbon atoms, a carbonamido group with 1 to 30 carbon atoms (for example, formamido, acetoamido, trifluoroacetoamido, benzoamido), a sulfonamido group with 1 to 30 carbon atoms (for example, methane sulfonamido, trifluoromethane sulfonamido, n-butane sulfonamido, p-toluene sulfonamido), a carbamoyl groups with 1 to 30 carbon atoms (for example, carbamoyl, N,N-dimethylcarbamoyl, N-methylcarbamoyl, pyrrolidinocarbonyl, N-n-hexadecylcarbamoyl), a sulfamoyl group with 0 to 30 carbon atoms (for example, sulfamoyl, N-methylsulfamoyl, N,N-dimethylsulfamoyl, morpholino sulfonyl, N-n dodecylsulfamoyl), a ureido group with 1 to 30 carbon atoms (for example, ureido, 3-methylureido, 3-phenylureido, 3,3-dimethylureido), an acyl group with 1 to 30 carbon atoms (for example, acetyl, pivaloyl, benzoyl, dodecanoyl), an acyloxy group with 1 to 30 carbon atoms (for example, acetoxy, benzoyl), an aliphatic oxy group with 1 to 30 carbon atoms, an aromatic oxy group with 6 to 30 carbon atoms, an aliphatic thio group with 1 to 30 carbon atoms, an aromatic thio group with 6 to 30 carbon atoms, an aliphatic sulfonyl group with 1 to 30 carbon atoms, an aromatic sulfonyl group with 6 to 30 carbon atoms, an aliphatic sulfinyl group with 1 to 30 carbon atoms, an aromatic sulfinyl group with 6 to 30 carbon atoms, an aliphatic oxy carbonyl group with 2 to 30 carbon atoms, an aliphatic oxy carbonyl group with 7 to 30 carbon atoms, an aliphatic oxy carbonylamino group with 2 to 30 carbon atoms, an aromatic oxy carbonylamino group with 7 to 30 carbon atoms, a sulfamoylamino group with 0 to 30 carbon atoms (for example, sulfamoylamino, 3,3-dimethylsulfamoylamino, piperidino sulfonylamino), a heterocyclic group with 1 to 30 carbon atoms, or an imido group with 4 to 30 carbon atoms (for example, succinimido, maleinimido, phthalimido, diglycolimido, 4-nitrophthalimido).

In Formula (I), R_3 represents a hydrogen or R_6Y, in which R_6 represents a hydrogen atom, an aliphatic group with 1 to 30 carbon atoms, an aromatic group with 6 to 30 carbon atoms, a heterocyclic group with 1 to 30 carbon atoms,



$$-OR_7,\ -SR_7,\ -COR_8,\ -N(R_9)(R_{10}),\ -PO(R_7)_2,\ -PO(-OR_7)_2,\ -PO\left(-N(R_9)(R_{10})\right)_2,\ -SO_2-N(R_9)(R_{10}),\ -CO_2R_7,$$

$-SO_2R_7$, $-SO_2OR_7$,

or an imido group with 4 to 30 carbon atoms (for example, succinimido, maleinimido, phthalimido, diacetylimido); Y represents, for example,

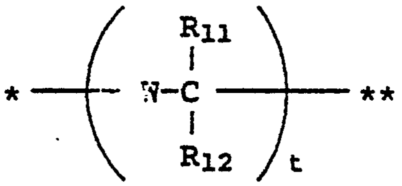
$>N-R_9$, -CO-, $-SO_2-$, -SO- or single bond, R_7 represents an aliphatic group with 1 to 30 carbon atoms, an aromatic group with 6 to 30 carbon atoms or a heterocyclic group with 1 to 30 carbon atoms; R_8 represents a hydrogen atom, an aliphatic group with 1 to 30 carbon atoms, aromatic group with 6 to 30 carbon atoms or a heterocyclic group with 1 to 30 carbon atoms; R_9 and R_{10} represent independently a hydrogen atom, an aliphatic group with 1 to 30 carbon atoms, an aromatic group with 6 to 30 carbon atoms, a heterocyclic group with 1 to 30 carbon atoms, an acyl group with 1 to 30 carbon atoms (for example, acetyl, trifluoroacetyl, benzoyl, p-chlorobenzoyl) or a sulfonyl group with 1 to 30 carbon atoms (for example, methane sulfonyl, n-butane sulfonyl, benzene sulfonyl, p-nitrobenzene sulfonyl). R_9 and R_{10} may join with each other to form a ring.

In Formula (I), the group represented by LINK may or may not be used in the present invention. It is better not used the group but it may be properly selected depending on the purposes. In the case of using the group represented by LINK, the following known functional linkage groups, etc. may be included:

(1) A group utilizing the cleavage reaction of a hemiacetal:

It is described, for example, in U.S. Patent 4,146,396 and JP-A-60-249148 and JP-A-60-249149 and represented by the following formula (in this case the symbol * represents the coupling active position of a coupler represented by Formula (I), that is, the position coupled to the 4-position of 1-naphthol, while the symbol ** represents the position bonding to S, that is, sulfur atom in Formula (I)):

Formula (T-1)

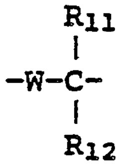


$$*-\left(W-\underset{R_{12}}{\overset{R_{11}}{C}}\right)_t-**$$

wherein W represents an oxygen atom, sulfur atom or

$$\underset{R_{13}}{-N-};$$

R_{11} and R_{12} each represents a hydrogen atom or substituent; R_{13} represents a substituent; t represents 1 or 2. If t is 2, each

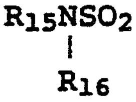


$$-W-\underset{R_{12}}{\overset{R_{11}}{\overset{|}{\underset{|}{C}}}}-$$

may be indentical to or different from the other. Typical examples of the Substituent suitable for use as R_{11}, R_{12}, or R_{13} are R_{15} group, $R_{15}CO$- group, $R_{15}SO_2$- group,

$$R_{15}\underset{\underset{R_{16}}{|}}{N}CO-$$

group or



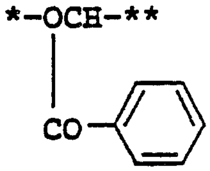
$$R_{15}\underset{\underset{R_{16}}{|}}{N}SO_2$$

group. In this case R_{15} represents an aliphatic group, an aromatic group or a heterocyclic group; R_{16} represents a hydrogen atom, an aliphatic group, an aromatic group or a heterocyclic group. R_{11}, R_{12}, R_{13} can represent a divalent group, and any two of R_{11}, R_{12} and R_{13} can be joined to form a cyclic structure. Specific examples of the group represented by the Formula (T-1) are set forth below. However, the present invention shall not be construed as being limited to these examples.

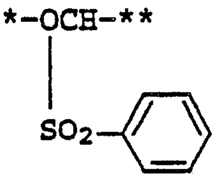
(T-1)1

$*-OCH_2-**$

(T-1)2



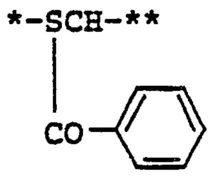
(T-1)3



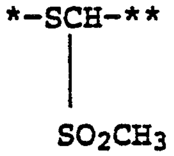
(T-1)4

$*-SCH_2-**$

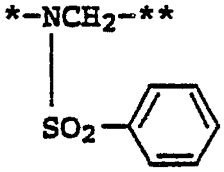
(T-1)5



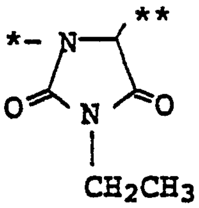
(T-1)6



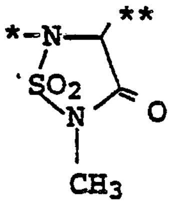
(T-1)7



(T-1)8



(T-1)9



(2) Groups causing cleavage reaction utilizing the intramolecular nucleophilic substitution reaction:

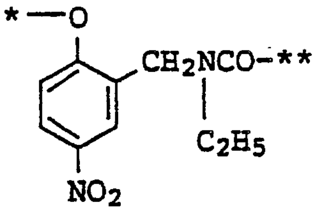
There can be mentioned a timing group, for example, described in U.S. Patent 4,248,962, which can be represented by the following Formula:

Formula (T-2)

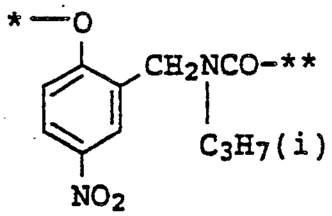
*-Nu-LINK-E-**

In the formula, Nu represents a nucleophilic group in which an oxygen atom or a sulfur atom is an example of the nucleophilic species; E represents an electrophilic group capable of cleaving the bonding with the symbol ** upon nucleophilic attack from Nu. LINK represents a linkage group for sterically relating Nu and E such that they can conduct an intramolecular nucleophilic substitution reaction. Specific examples of the groups represented by Formula (T-2) are described below, but the present invention not be construed as being limited thereto.

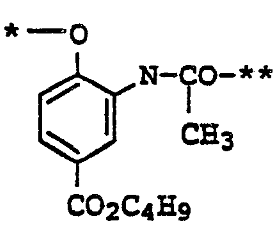
(T-2)1



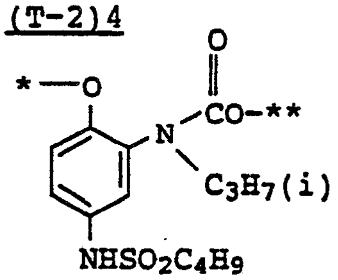
(T-2)2



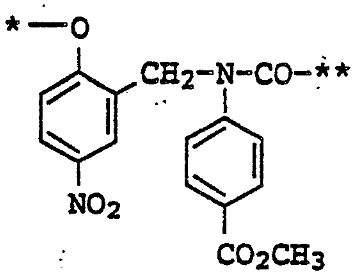
(T-2)3



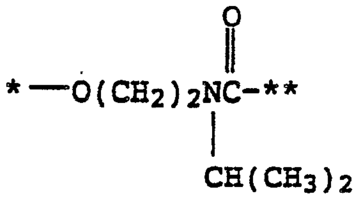
(T-2)4



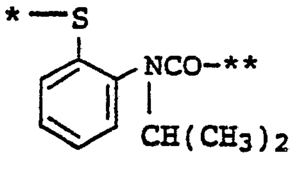
(T-2)5



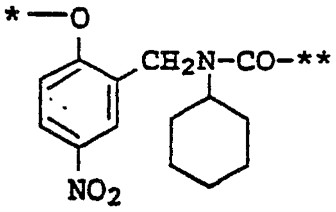
(T-2)6



(T-2)7



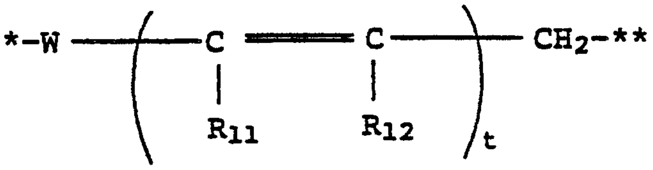
(T-2)8



(3) Groups causing cleavage reaction utilizing the electron transfer reaction along the conjugated system:

They are described, for example, in U.S. Patents 4,409,323 and 4,421,845, JP-A-57-188035, JP-A-58-98728, JP-A-58-209736, JP-A-58-209738 and JP-A-58-209738 and represented by Formula (T-3).

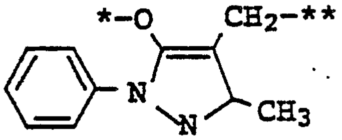
Formula (T-3)



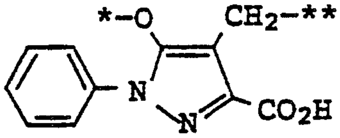
$$*\text{-}W\text{-}\left(\underset{R_{11}}{C}=\underset{R_{12}}{C}\right)_t\text{-}CH_2\text{-}**$$

wherein the symbol *, the symbol **, W, R_{11}, R_{12} and t have the same meanings as explained for Formula (T-1), provided that R_{11} and R_{12} may join with each other to form a constituent for a benzene ring or a heterocyclic ring. Specific examples can include the following groups.

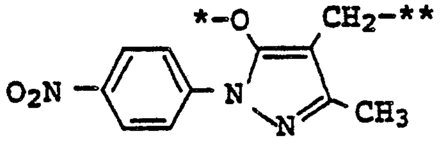
(T-3)1



(T-3)2

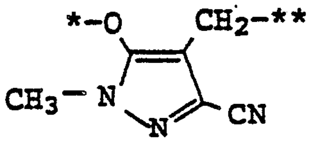


(T-3)3

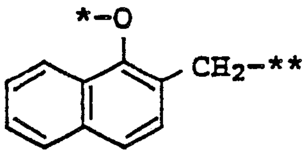


(T-3)4

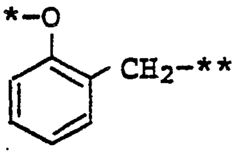
(T-3)5



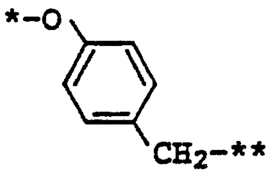
(T-3)6



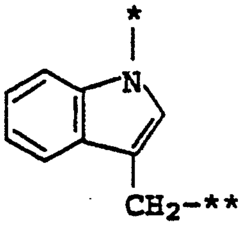
(T-3)7



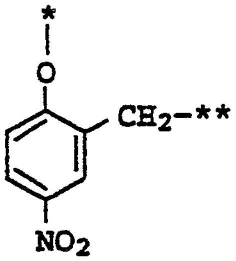
(T-3)8



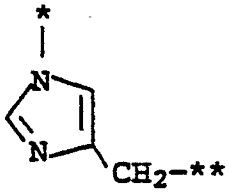
(T-3)9



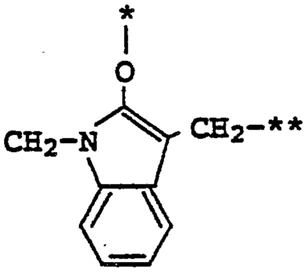
(T-3)10



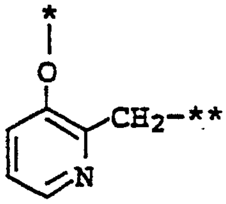
(T-3)11



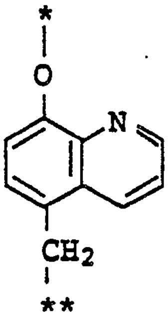
(T-3)12



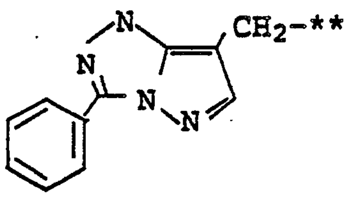
(T-3)13



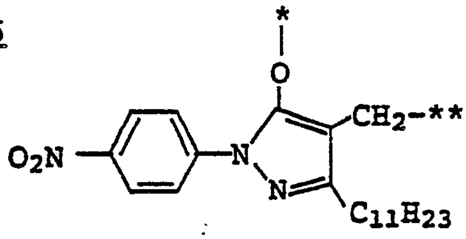
(T-3)14



(T-3)15



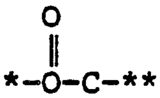
(T-3)16



(4) Groups utilizing the cleavage reaction due to ester hydrolysis:

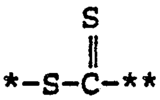
They are linkage groups described, for example, in West German Patent Application (OLS) No. 2,626,315 and can include the following groups. In the formula the symbol * and the symbol ** have the same meanings as those explained for Formula (T-1).

Formula (T-4)



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

Formula (T-5)

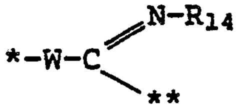


$$*-S-\overset{\overset{S}{\parallel}}{C}-**$$

(5) Groups utilizing the cleavage reaction of the imino ketal group

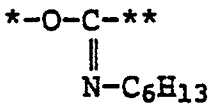
They are linkage groups, for example, described in U.S. Patent 4,546,073 and represented by the following formula.

Formula (T-6)

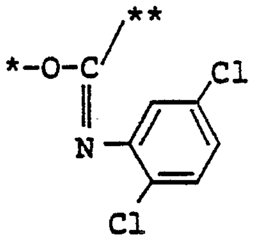


wherein the symbol *, the symbol ** and W have the same meanings as those for the Formula (T-1), R_{14} has the same meanings as for R_{13} of Formula (T-1). Specific examples of the groups represented by the general formula (T-6) can include the following groups, but the present invention is not to be construed as being limited thereto:

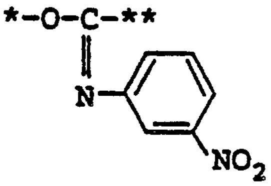
(T-6)1



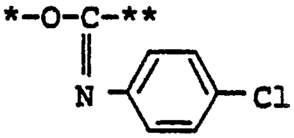
(T-6)2



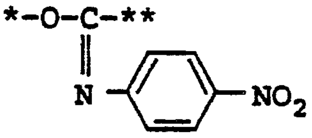
(T-6)3



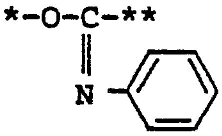
(T-6)4



(T-6)5



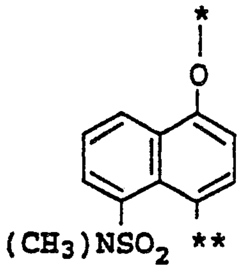
(T-6)6



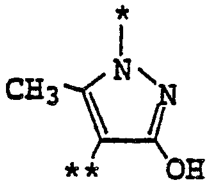
(6) Groups that function as a coupler or reducing agent after coupling reaction (e.g., hydroquinone, catechol, pyrogallol, aminophenol derivative, etc.) and carry out releasing by the coupling reaction or redox reaction:

They are described, for example, in U.S. Patent 4,438,193 and 4,618,571, and JP-A-60-203943, JP-A-60-213944 and JP-A-61-236551 and specific examples can include the following groups, but the present invention is not to be construed as being limited thereto.

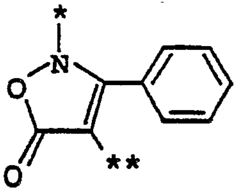
C1



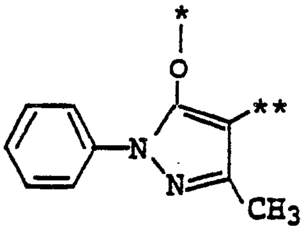
C2



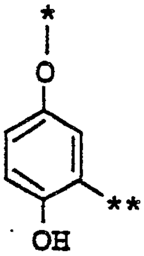
C3



C4



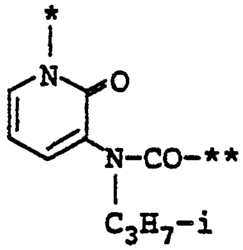
C5



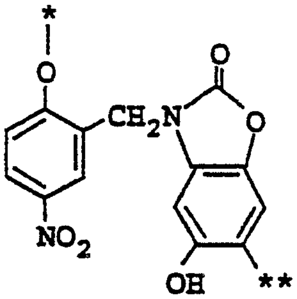
(7) Groups having in combination for one or more of the mechanisms of (1) to (6):

They are described, for example, in JP-A-57-56837, JP-A-60-214358, JP-A-60-218645, JP-A-60-229030 and JP-A-61-156217 and specific examples can include the following groups, the present invention not being limited thereto:

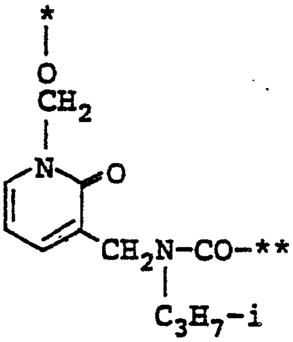
COM-1



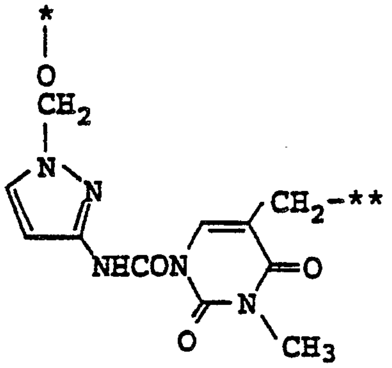
COM-2



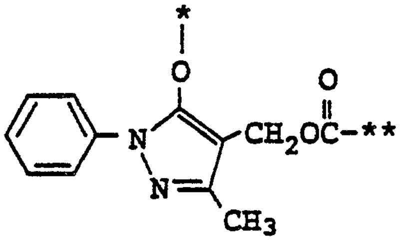
COM-3



COM-4



COM-5



In Formula (I), L represents a (n+1) valent group, that is, those groups formed by removing n number of hydrogen atoms from linear, branched or cyclic alkyl group with 1 to 8 carbon atoms, an aromatic group with 6 to 10 carbon atoms which may be substituted with a halogen atom or an alkyl group, or a heterocyclic group with 1 to 10 carbon atoms (for example, tetrazol-1-yl, 1,3,4-triazol-1-yl, 2-methyl-1,3,4-triazol-1-yl, 1,3,4-thiadiazol-2-yl, 1,3;4 oxadiazol-2-yl, 1,3,4 triazol-2-yl, 1-methyl-1,3,4-triazol-2-yl, thiazol-2-yl, oxazol-2-yl, imidazol-2-yl, 1-methylimidazol-2-yl, pyrimidin-2-yl respectively); X represents a water soluble substituent, and n represents an integer of 1 to 3.

In Formula (I), the groups represented by X are those groups with not more than 8 carbon atoms, for example, carboxyl group, sulfo group, hydroxyl group, amino group, alkoxy group, carbonamido group, sulfonamido group, carbamoyl group, sulfamoyl group, ureido group, sulfamyl group, acryl group, amidino group, alkylsulfonyl group, phosphono group, phosphonooxy group, or those groups containing at least one of these of aforementioned groups.

In Formula (I), R_2 and R_3 or a plurality of R_2 may join with each other to form a ring. Examples of R_2 and R_3 joined with each other can include: $-CH_2CO-$, $-OCO-$, $-NHCO-$, $C(CH_3)_2CO$ and $-CH=CHCO-$. Examples of a plurality of R_2 joined with each other can include $-(CH_2)_4-$, $-OCO-$, $-OCONH$, $-NHCONH-$, $-(CH=CH)_2-$, $-OCH_2O-$, $-OCH_2CH_2O-$, $-OC(CH_3)_2O-$, etc.

Examples of preferred substituents in the compound represented by Formula (I) are described below.

In Formula (I), R is preferably a halogen atom, $-COR_4$ or $-SO_2R_4$, and the case in which R_4 represents an amino group is further preferred.

Examples of $-COR_4$ can include, carbamoyl, N-ethylcarbamoyl, N-n-butylcarbamoyl, N-cyclohexylcarbamoyl, N-(2-ethylhexyl)carbamoyl, N-dodecylcarbamoyl, N-hexadecylcarbamoyl, N-(3-decyloxypropyl) carbamoyl, N-(3-dodecyloxypropyl)carbamoyl, N-(3-(2,4-di-t-pentylphenoxy)propyl)carbamoyl, N-(4-(2,4-di-t-pentylphenoxy)butyl)carbamoyl, N,N-dimethylcarbamoyl, N,N-dibutylcarbamoyl, N-methyl-N-dodecylcarbamoyl, morpholinocarbonyl, N-methyl-N-phenylcarbamoyl, N-(2-tetradecyloxyphenyl)carbamoyl, N-phenylcarbamoyl, N-(4-tetradecyloxyphenyl)carbamoyl, N-(2-propoxyphenyl)carbamoyl, N-(2-chloro-5-dodecyloxyphenyl)carbamoyl and N-(2-chlorophenyl)carbamoyl. Examples of $-SO_2R_4$ can include sulfamoyl, N-methylsulfamoyl, N,N-diethylsulfamoyl, N,N-diisopropylsulfamoyl, N-(3-dodecyloxypropyl)sulfamoyl, N-(3-(2,4-di-t-pentylphenoxy)propyl)sulfamoyl, N-(4-(2,4-di-t-pentylphenoxy)butyl)sulfamoyl, pyrrolidinosulfonyl, N-phenylsulfonyl, N-(2-butoxyphenyl)sulfamoyl and N-(2-tetradecyloxyphenyl)sulfamoyl. As R_1, $-COR_4$ in which R_4 is an amino group is particularly preferred.

For $(R_2)_\ell$ in Formula (I) $\ell=1$ is desirable and $\ell=0$ is even more desirable. When $\ell=1$, R_2 is preferably a halogen atom, an aliphatic group, an aliphatic oxy group, a carbonamido group, a sulfonamido group, a cyano group, etc.; a fluorine atom, a chlorine atom, a trifluoromethyl group, a methoxy group or a cyano group being particularly preferred. The substitution position of R_2 is preferably at the 2-position of the 4-position relative to R_3NH-.

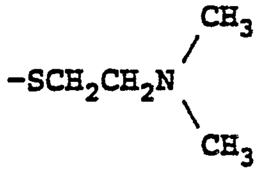
In a case where R_3 in Formula (I) is represented by R_6Y, R_6 is preferably an aliphatic group, an aromatic group, $-OR_7$ or $-SR_7$; Y is preferably -CO- or $-SO_2$. Examples of the aliphatic group can include: e.g., methyl, trifluoromethyl, trichloromethyl, ethyl, heptafluoropropyl, t-butyl, 1-ethylpentyl, cyclohexyl, benzyl, undecyl, tridecyl and 1-(2,4-di-t-pentylphenoxy)propyl. Examples of the aromatic group can include: e.g., phenyl, 1-naphthyl, 2-naphthyl, 2-chlorophenyl, 4-methoxyphenyl, 4-nitrophenyl and pentafluorophenyl. Examples of $-OR_7$ can include: e.g., methoxy, ethoxy, isopropoxy, n-butoxy, isobutoxy, t-butoxy, n-pentyloxy, n-hexyloxy, n-octyloxy, 2-ethylhexyloxy, n-decyloxy, n-dodecyloxy, 2-methoxyethoxy, benzyloxy, trichloroethoxy, trifluoroethoxy, phenoxy and p-methylphenoxy. Examples of $-SR_7$ can include: e.g., methylthio, ethylthio, allylthio, n-butylthio, benzylthio, n-dodecylthio, phenylthio, p-t-octylphenylthio, p-dodecylphenylthio, and p-octyloxyphenylthio. R_3 is, more preferably, an aliphatic oxy carbonyl group in which R_6 is R_7O and Y is -CO-, or an aliphatic or aromatic sulfonyl group in which R_6 is an aliphatic or aromatic group and Y is $-SO_2$-. R_3 is most preferably an aliphatic oxy carbonyl group.

In Formula (I), LINK is preferably represented in Formula (T-1), (T-2) or (T-3) described above, but it is generally preferred when m = 0, that is, not using the functional connection group.

In Formula (I), L is preferably an alkylene group or heterocyclic group, more preferably, an alkylene group.

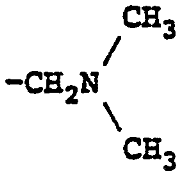
In Formula (I), X is, preferably, a substituent in which π-substituent constant is 0.5 or less, preferably, the substituent constant has a negative value. The value is determined by the method as described in "Substituent Constants for Correlation Analysis in Chemistry and Biology" written by C. Hansch and A. Leo, published by John Wiley, 1979. Examples of X and π-substituent constants (within ( )) are shown below.

$-CONH_2$(-1.49),
$-COOH$ (-0.32),
$-COCH_3$ (-0.55),
$-NHCOCH_3$ (-0.97),
$-CH_2CH_2COOH$ (-0.29),
$-CH_2CH_2NH_2$ (0.08),
$-SCH_2COOH$ (-0.31,



$-SCH_2CH_2N(CH_3)_2$ (0.43),

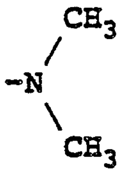
$-CH_2COOH$ (-0.68),
$-SCH_2CONH_2$ (-0.97),
$-SCH_2COCH_3$ (0.43),
$-SCH_2CH_2CO_2H$ (-0.01),
$-OH$ (-0.67),
$-CONHOH$ (-0.38),
$-CH_2OH$ (-1.03),
$-CN$ (-0.57),
$-CH_2CN$ (-0.57),
$-CH_2NH_2$ (-1.04),



$-CH_2N(CH_3)_2$ (-0.15),

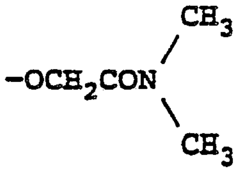
$-NH_2$ (-1.23),

$-NHCHO$ (-0.98),
$-NHCONH_2$ (-1.30),
$-NHCH_3$ (-0.47),
$-NHSO_2CH_3$ (-1.18),

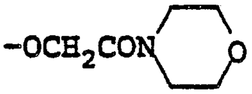


$-N(CH_3)_2$ (0.18),

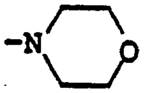
$-N(SO_2CH_3)_2$ (-1.51),
$-OCONH_2$ (-1.05),
$-OCH_3$ (-0.02),
$-OSO_2CH_3$ (-0.88),
$-OCOCH_3$ (-0.64),
$-OCH_2COOH$ (-0.87),
$-SO_2NH_2$ (-1.82),
$-SO_2CH_3$ (-1.63),
$-OCH_2CONH_2$ (-1.37),



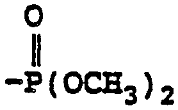
$-OCH_2CON(CH_3)_2$ (-1.36),



(-1.39),



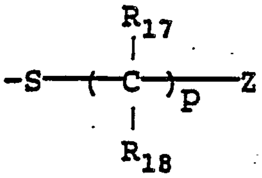
(-0.77),



$-P(=O)(OCH_3)_2$ (-1.18),

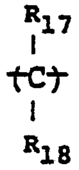
In Formula (I), n is preferably 1 or 2 and, more preferably, 1.
Further in Formula (I), most preferred $-S-L-(X)_n$ is represented by the following Formula (II):

Formula (II):



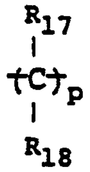
$$-S-(C(R_{17})(R_{18}))_p-Z$$

wherein R_{17} and R_{18} represent a hydrogen atom or an alkyl group with 1 to 4 carbon atoms, p represents an integer of 1 to 8, and Z represents a hydroxyl group, a carboxyl group, a sulfo group or an amino group with 0 to 8 carbon atoms (for example, amino, methylamino, ethylamino, methoxyethylamino, butylamino, dimethylamino, diethylamino, dipropylamino, diisopropylamino, dibutylamino, diisobutylamino, piperidino, pyrrolidino, morpholino). In a case where p represents an integer of 2 to 8, each



$$\left(\underset{\underset{R_{18}}{|}}{\overset{\overset{R_{17}}{|}}{C}}\right)$$

may be identical to or different from the others, and the number Of carbon atoms in



$$\left(\underset{\underset{R_{18}}{|}}{\overset{\overset{R_{17}}{|}}{C}}\right)_p$$

is from 1 to 8. Among the groups represented by Z, the carboxyl group is particularly preferred.

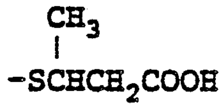
In Formula (I), examples of S-L-$(X)_n$ are shown below, the present invention not being limited thereto:

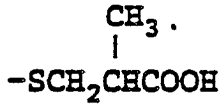
S1 $-SCH_2COOH$

S2 $-SCH_2CH_2COOH$

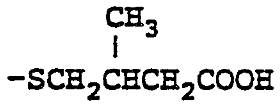
S3 $-SCH_2CH_2CH_2COOH$

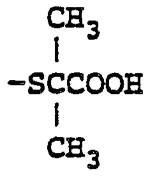
S4 
$-S\overset{\displaystyle CH_3}{\overset{|}{C}}HCOOH$

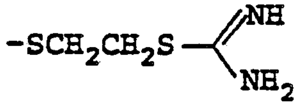
S5 
$-S\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2COOH$

S6 
$-SCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCOOH$

S7 $-S(CH_2)_4COOH$

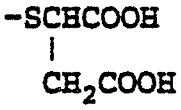
S8 
$-SCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2COOH$

S9 
$-S\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}COOH$

S10 

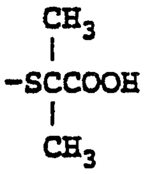
S11 $-SCH_2CH_2OCH_2CH_2COOH$

S12



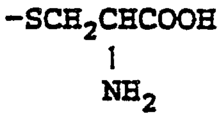
$-SCH(COOH)CH_2COOH$

S13



$-SC(CH_3)_2COOH$

S14



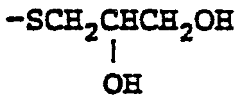
$-SCH_2CH(NH_2)COOH$

S15 $-SCH_2CH_2OH$

S16 $-SCH_2CH_2CH_2OH$

S17 $-SCH_2CH_2OCH_2CH_2OH$

S18

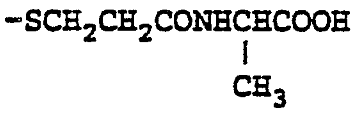


$-SCH_2CH(OH)CH_2OH$

S19 $-SCH_2CH_2SO_3Na$

S20 $-SCH_2CH_2CONHCH_2COOH$

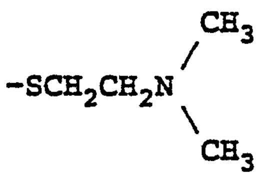
S21



$-SCH_2CH_2CONHCH(CH_3)COOH$

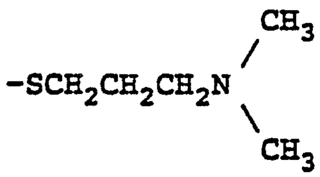
S22 $-SCH_2CH_2NH_2$

S23

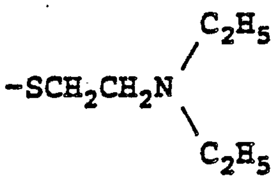


$-SCH_2CH_2N(CH_3)_2$

S24



$-SCH_2CH_2CH_2N(CH_3)_2$

S25


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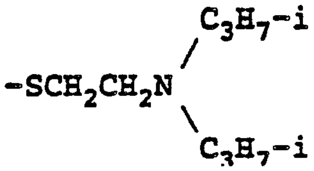
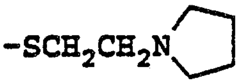


S27


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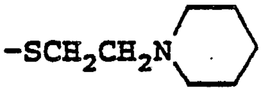
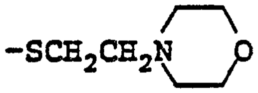


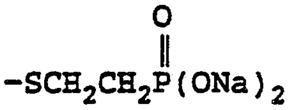
S29


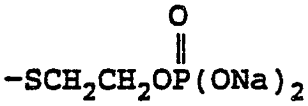
S30 $-SCH_2CH_2NHCH_3$

S31 $-SCH_2CH_2NHCOCH_3$

S32 $-SCH_2CH_2NHSO_2CH_3$

S33 $-SCH_2CH_2NHCOOCH_3$

S34

$-SCH_2CH_2\overset{O}{\overset{\|}{P}}(ONa)_2$

S35

$-SCH_2CH_2O\overset{O}{\overset{\|}{P}}(ONa)_2$

S36 $-SCH_2CH_2SCH_2COOH$

S37 $-SCH_2CH_2CN$

S38 $-SCH_2CH_2CH_2SO_3Na$

S39 $-SCH_2CH_2CONH_2$

S40 $-SCH_2CH_2SO_2CH_3$

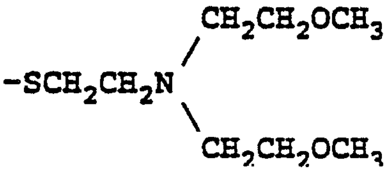
S41 $-SCH_2CH_2OCH_3$

S42 $-SCH_2CH_2CH_2SO_3Na$

S43 $-SCH_2CH_2SO_2NH_2$

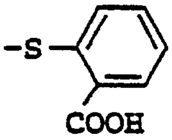
S44 $-SCH_2CH_2SCH_2CH_2OH$

S45



$-SCH_2CH_2N(CH_2CH_2OCH_3)_2$

S46



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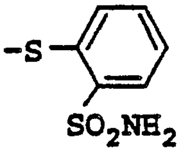

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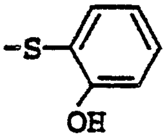

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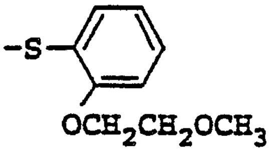

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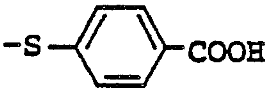
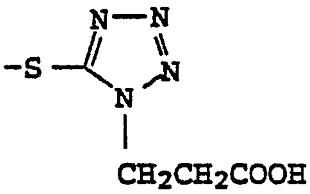


S51



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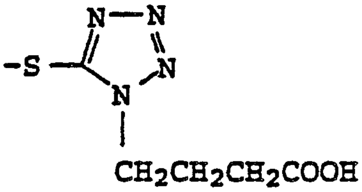

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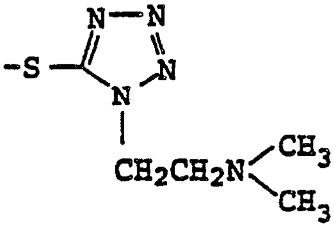

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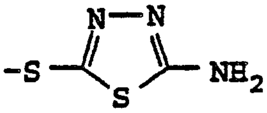

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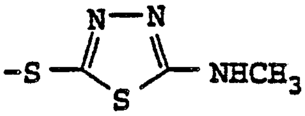

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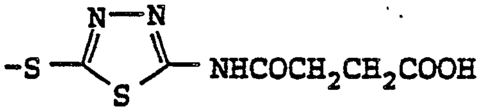

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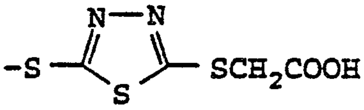
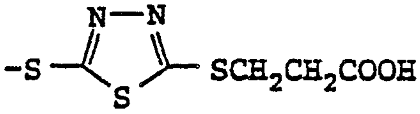
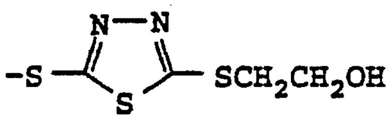


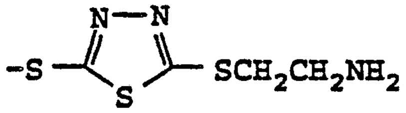
S58



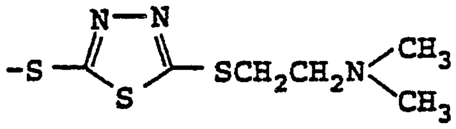
S59



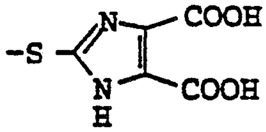
S60



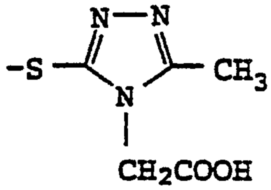
S61



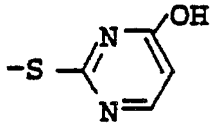
S62



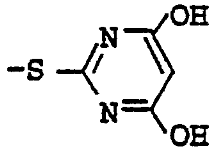
S63



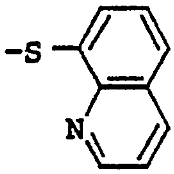
S64



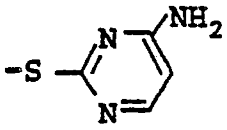
S65



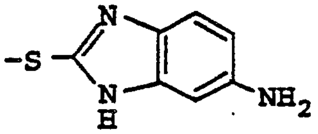
S66



S67



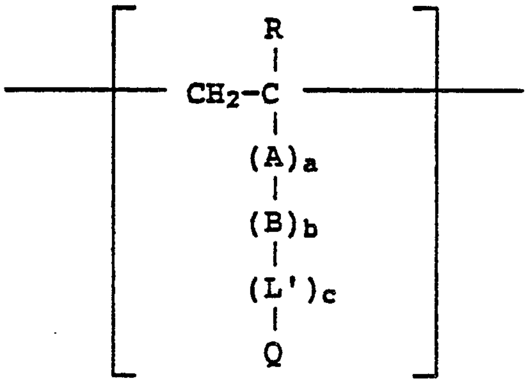
S68



The coupler represented by Formula (I) may form a dimer or higher polymer jointed with another by way of divalent or higher valent groups at the substituents R_1, R_2 and R_3 respectively. In this case, the range for the number of carbon atoms shown for each of the substituents as described above may beyond the scope of the above definition.

In the case where the coupler represented by the Formula (I) forms a polymer, typical examples thereof include a homopolymer or copolymer of addition polymerizable ethylenically unsaturated compounds having cyan dye forming coupler residue (cyan color forming monomer). In this case, the polymer contains repeating units of Formula (III) and one or more of cyan color-forming repeating units represented by Formula (III) may be contained in the polymer and it may be a copolymer containing one or more of the non-color-forming ethylenic monomer as the copolymerization ingredient.

Formula (III):



$$\left[-CH_2-\underset{\underset{\underset{\underset{Q}{|}}{(L')_c}}{\underset{|}{(B)_b}}}{\underset{|}{\underset{(A)_a}{|}}}}{\overset{R}{\overset{|}{C}}}- \right]$$

wherein R represents a hydrogen atom, an alkyl group with 1 to 4 carbon atoms or a chlorine atom; A represents -CONH-, -COO- or a substituted or unsubstituted phenylene group; B represents a substituted or unsubstituted alkylene group, a phenylene group or an aralkylene group; L' represents -CONH-, -NHCONH-, -NHCOO-, -NHCO-, -OCONH-, -NH-, COO-, -OCO-, -CO-, -O-, $-SO_2-$, $-NHSO_2-$ or $-SO_2NH-$. a, b, c represents 0 or 1. Q represents a cyan coupler residue formed by removing other hydrogen atoms than the hydrogen atom at the hydroxy group on 1-position from the compound represented by Formula (I).

As the polymer, a copolymer of the cyan color forming monomer giving the coupler unit of Formula (III) with the following non-color-forming ethylenic monomer is preferred.

The non-color-forming ethylenic monomer, which is not coupled with oxidation products of an aromatic primary amine developing agent, can include: acrylic acid; α-chloroalkylacrylic acid; α-alkylacrylic acid (for example, methacryl acid), esters or amides derived from these acrylic acids (for example, acrylamide, methacrylamide, n-butylacrylamide, t-butylacrylamide, diacetoneacrylamide, N-methylolacrylamide, N-(1,1-

dimethyl-2-sulfonatoethyl)acrylamide, N-(3-sulfonatopropyl)acrylamide, methylacrylate, ethylacrylate, n-propylacrylate, n-butylacrylate, t-butylacrylate, isobutylacrylate, acetoacetoxyethylacrylate, n-hexylacrylate, 2 ethylhexylacrylate, n-octylacrylate, laurylacrylate, methylmethacrylate, ethylmethacrylate, n-butylmethacrylate, β-hydroxymethacrylate); vinyl esters (for example, vinyl acetate, vinyl propionate, vinyl laurate); acrylonitrile; methacrylonitrile; aromatic vinyl compound (for example, styrene and derivatives thereof such as vinyltoluene, divinyl benzene, potassium styrene sulfinate, vinyl acetophenone, sulfostyrene); itaconic acid; citraconic acid; crotonic acid; vinylidene chloride; vinylalkyl ether (for example, vinylethyl ether, maleic acid esters, N-vinyl-2-pyrrolidone, N-vinyl pyridine, 2- and 4-vinyl pyridine).

Acrylic acid ester, methacrylic acid ester and maleic acid esters are particularly preferred. Two or more of the non-color forming ethylenic monomers can be used together. For instance, the following combinations can be used: methyl acrylate and butyl acrylate, butyl acrylate and styrene, butyl methacrylate and methacrylic acid, methylacrylate and diacetone acrylamide, N-(1,1-dimethyl-2-sulfonatoethyl)acrylamide and acrylic acid, potassium styrene sulfinate and N-vinylpyrrolidone.

As is well-known in the field of the polymer coupler, the ethylenically unsaturated monomer for copolymerization with a vinylic monomer corresponding to Formula (III) described above can be selected such that preferred effect can be given to the copolymer formed with respect to physical properties and/or chemical properties of the copolymer, such as solubility, compatibility with a binder for the photographic colloid composition (for example, gelatin), flexibility, heat stability, etc.

For obtaining an oleophilic polymer coupler soluble in organic solvent, it is preferred to select, as the copolymerization ingredient, mainly, oleophilic non-color-forming ethylenic monomer, for example, acrylic acid ester, methacrylic acid ester, maleic acid ester, vinyl benzene).

The emulsion of the cyan polymer coupler for use in this invention may be prepared by emulsion-dispersing a solution of the oleophilic coupler obtained by the polymerization of the vinylic monomer giving the coupler unit dissolved in an organic solvent in an aqueous gelatin solution as the form of latex or may be prepared by a direct emulsion polymerization method.

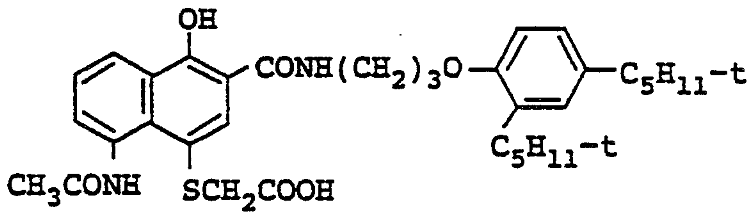
For emulsion dispersing the oleophilic polymer coupler in an aqueous gelatin solution as the form of latex, the mehtod described in U.S. Patent 3,451,820 can be used and for the emulsion polymerization, the method described in U.S. Patents 4,080,211 and 3,370,952 can be used.

For obtaining a hydrophilic polymer coupler soluble in neutral or alkaline water, it is preferred to use, as a copolymerization ingredient, those hydrophilic non color forming ethylenic monomer such as N-(1,1-dimethyl-2-sulfonatoethyl)acrylamide, 3-sulfonate propylacrylate, sodium styrenesulfonate, potassium 2-styrene sulfinate, propylacrylate, methacrylamide, acrylic acid, methacrylic acid, N-vinylpyrrolidone and N-vinylpyridine.

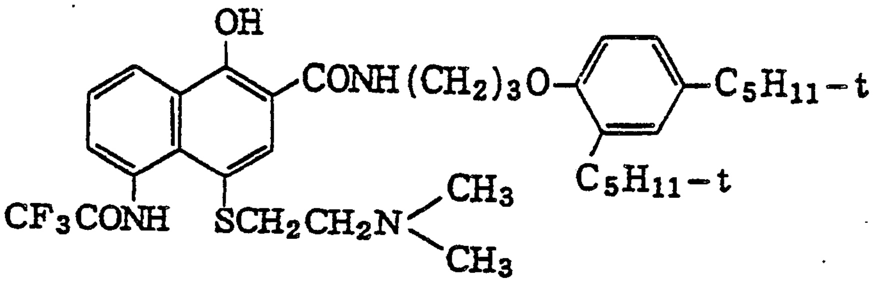
The hydrophilic polymer coupler can be added as an aqueous solution to a coating liquid, and it is also possible to add after being dissolved in a mixed solvent of water miscible organic solvent such as lower alcohol tetrahydrofuran, acetone, ethyl acetate, cyclohexane, ethyl lactate, dimethyl formamide or dimethylacetoamide and water. Further, the coupler may be added after being dissolved in an aqueous alkali solution or alkali-containing organic solvent. Furthermore, a small amount of surface active agent may be added.

Specific examples of the coupler represented by Formula (I) used in the present invention are to be shown below, but the invention is not to be construed as being limited thereto.

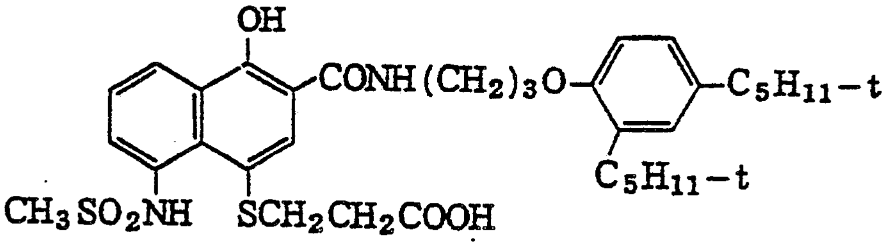
(1)



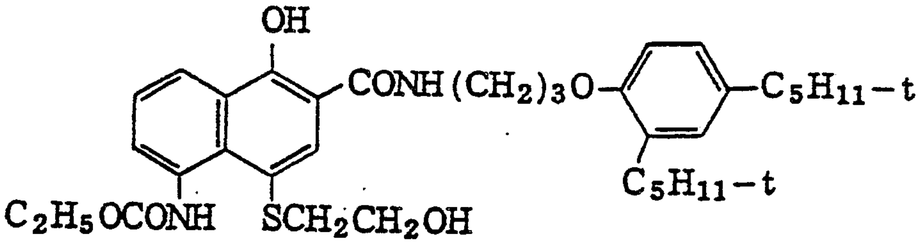
(2)


OH
CONH(CH2)3O
C5H11-t
C5H11-t
CF3CONH
SCH2CH2N
CH3
CH3

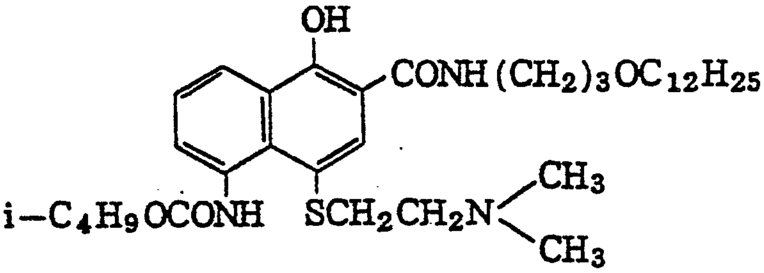
(3)


OH
CONH(CH2)3O
C5H11-t
C5H11-t
CH3SO2NH
SCH2CH2COOH

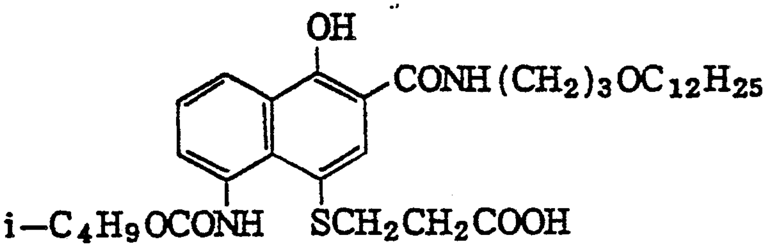
(4)


OH
CONH(CH2)3O
C5H11-t
C5H11-t
C2H5OCONH
SCH2CH2OH

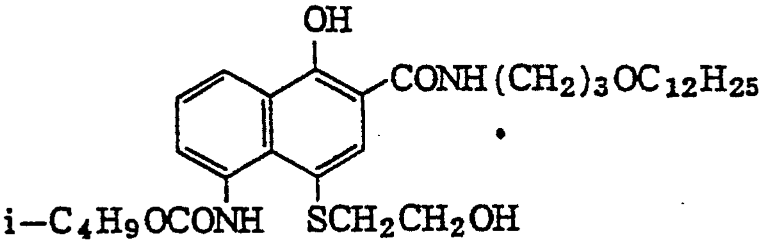
(5)


OH
CONH(CH2)3OC12H25
i-C4H9OCONH
SCH2CH2N
CH3
CH3

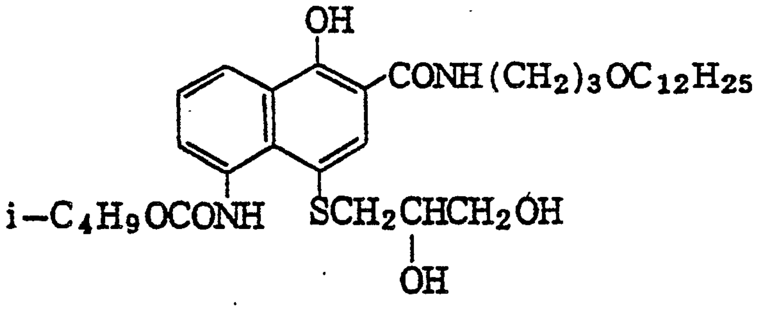
(6)


OH
CONH(CH2)3OC12H25
i-C4H9OCONH
SCH2CH2COOH

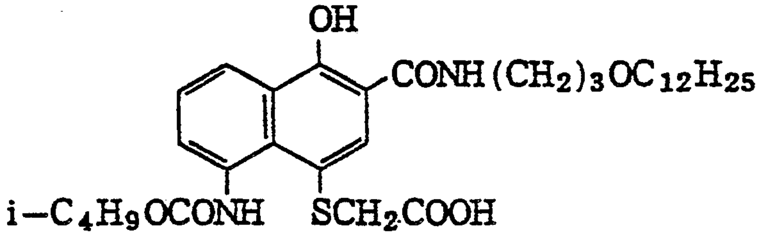
(7)


OH
CONH(CH2)3OC12H25
i-C4H9OCONH
SCH2CH2OH

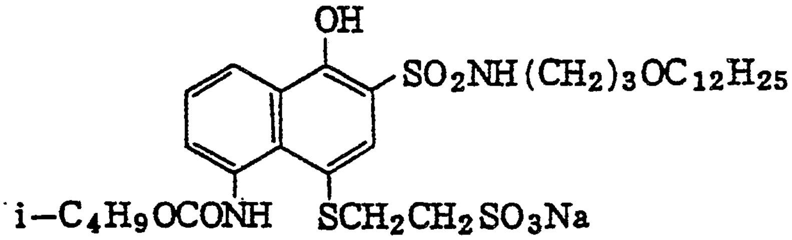
(8)


OH
CONH(CH2)3OC12H25
i–C4H9OCONH
SCH2CHCH2OH
OH

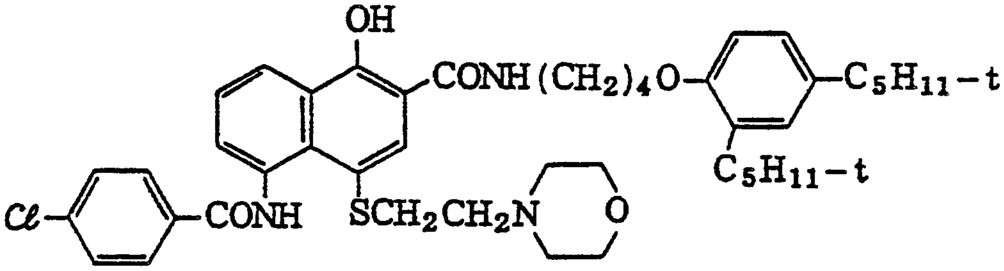
(9)


OH
CONH(CH2)3OC12H25
i–C4H9OCONH
SCH2COOH

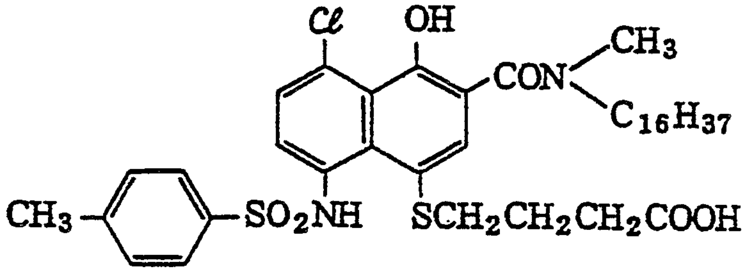
(10)


OH
SO2NH(CH2)3OC12H25
i–C4H9OCONH
SCH2CH2SO3Na

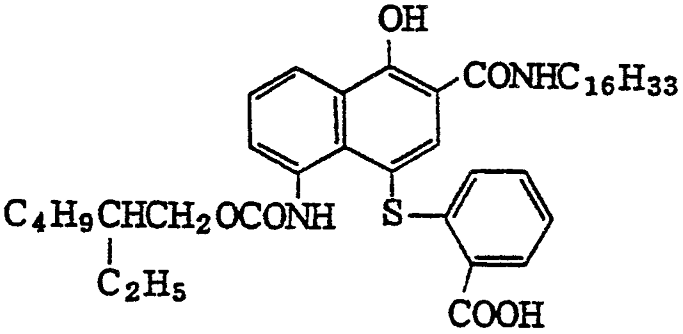
(11)



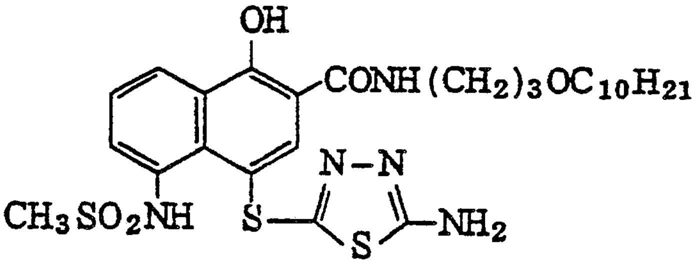
(12)



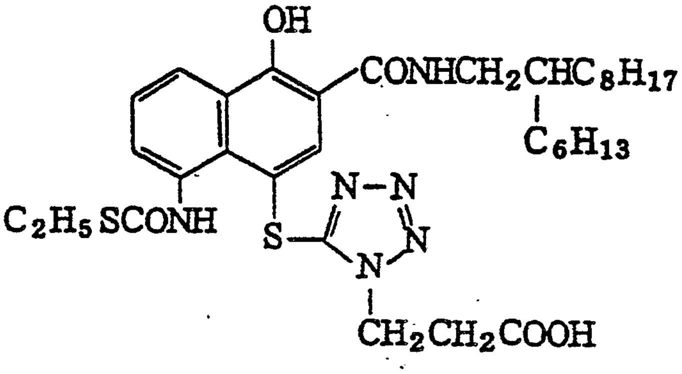
(13)



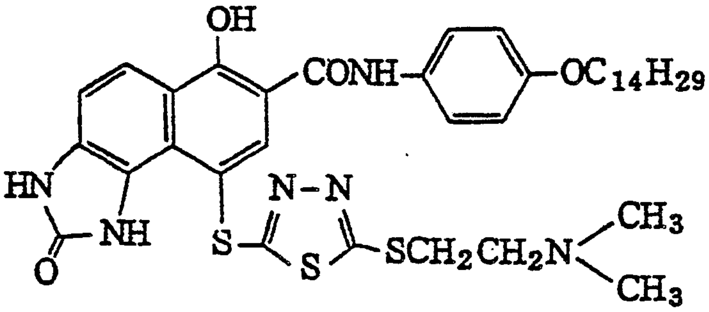
(14)



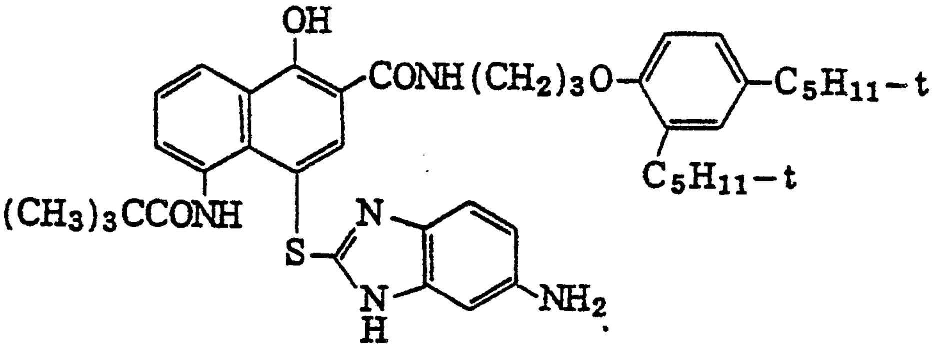
(15)



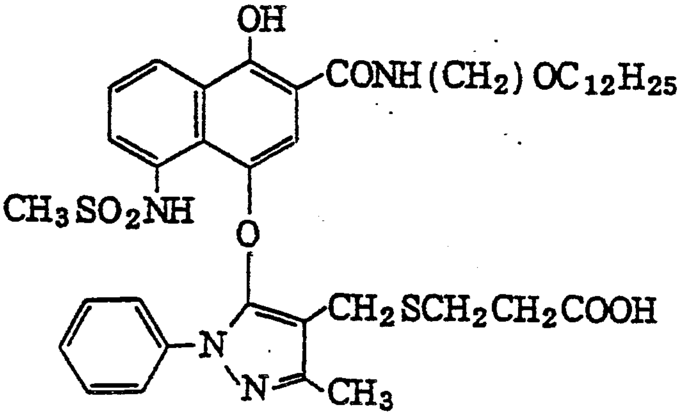
(16)



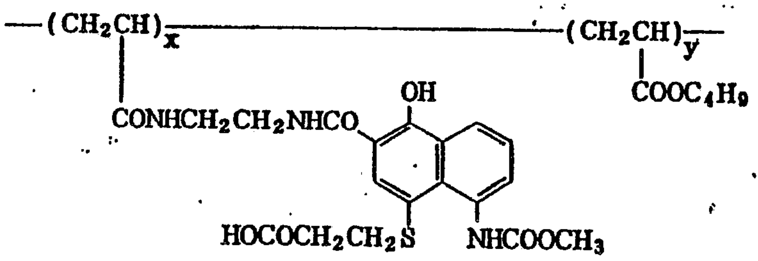
(17)


OH
CONH(CH2)3O
C5H11-t
C5H11-t
(CH3)3CCONH
S
N
N
H
NH2

(18)

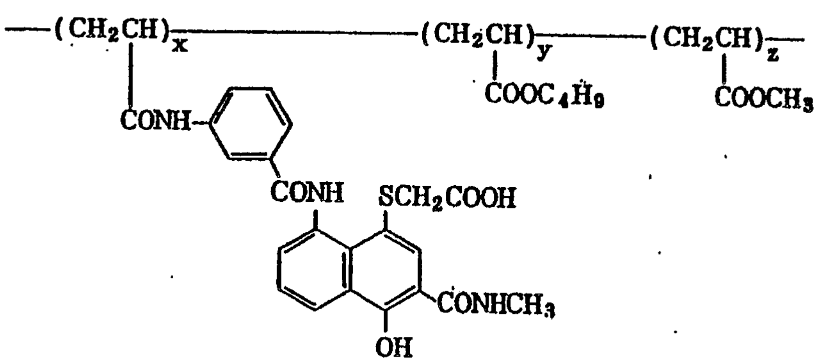

OH
CONH(CH2)OC12H25
CH3SO2NH
O
CH2SCH2CH2COOH
N
N
CH3

(19)



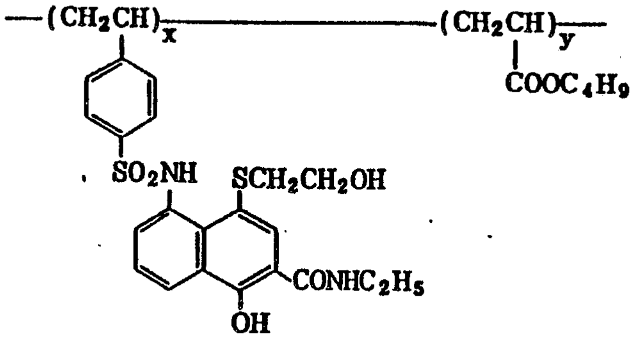
x / y = 50 / 50 (weight ratio)

(20)



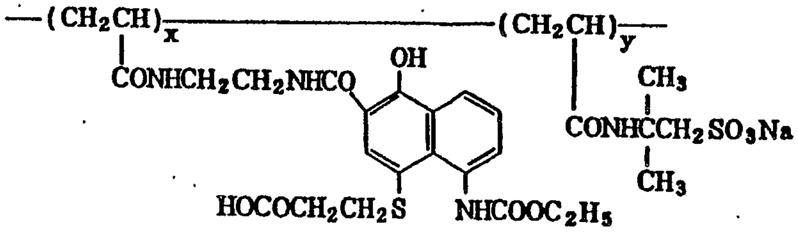
x / y / z = 50 / 25 / 25

(21)



x / y = 50 / 50

(22)

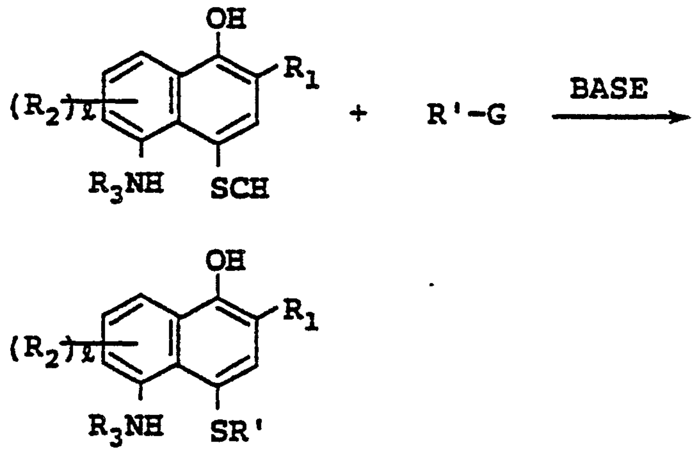


x / y = 45 / 55

The compounds represented by Formula (I) can be synthesized according to the method, for example, as described in EP-A-161626, and JP-A-61-201247, etc. Further, the compound having the functional linkage group can be synthesized according to the methods as described in those patent literatures set forth above for the explanation of the functional linkage groups, for example, U.S. Patents 4,146,396, 4,246,962, 4,409,323 and 4,421,845.

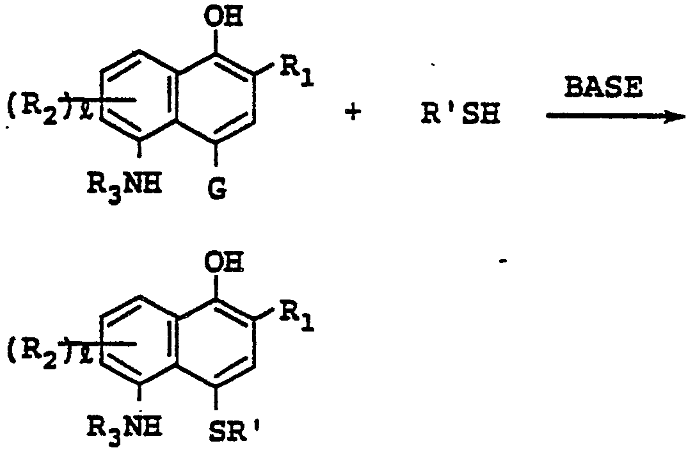
General synthesizing methods for the compounds not containing timing groups are described below. The compounds represented by Formula (I) used in the present invention can be synthesized by the methods shown below as (1), (2), (3).

(1) Tioetherifying reaction of 4 mercapto-1-naphthols under the presence of base:



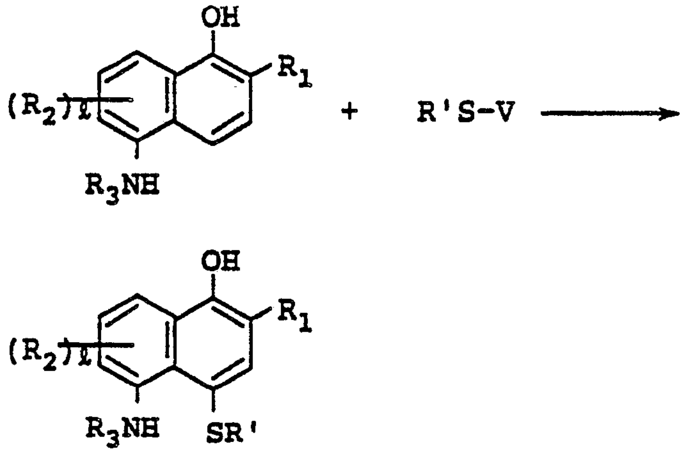
R′ represents -L-$(X)_n$ or a precursor thereof and G represents a group capable of splitting by a nucleophilic substitution reaction, for example, a halogen atom, a nitro group, a sulfonyl group and a sulfonyloxy group.

(2) Nucleophilic substitution reaction between 4-halogeno 1-naphthols and mercaptans under the presence of a base:



In the formula G and R′ have the same meanings as those for G and R′ in (1) above.

(3) Reaction between 1-naphthols and sulfenyl halide, sulfene amide, sulfene imide, disulfide, thiuram disulfide, thiol sulfonic acid ester, etc:



wherein R' has the same meaning as R' in (I) above and V represents a halogen atom, an amino group, an imido group, an alkyl, an aryl or a heterocyclic thio group, an amidinothio group or sulfonyl group, etc.

Synthetic examples are shown below, but the present invention is not to be construed being limited thereto.

Synthesis Example

Synthesis of Exemplified Compound (5)

5-isobutoxycabonylamino-1-hydroxy-N-(3-dodecyloxy propyl)-2-naphthoamide was dissolved by 26.4 g into 300 ml of methylene chloride and cooled to 0 °C, to which 6.8 g of sulfuryl chloride was dropped under stirring for about 10 min. After stirring for one hour, the solution of methylene chloride was washed with 300 ml of water and then concentrated under a reduced pressure. 8.5 g of N,N-dimethylaminoethanethiol hydrochloride, 30 g of potassium carbonate and 400 ml of N,N-dimethylformamide were added to the residue and then heated under reflux for 3 hours under a nitrogen gas stream. The reaction solution was cooled, 300 ml of ethyl acetate was added and extracted after neutralization. After sufficiently washing the ethylacetate solution with water, it was concentrated and fractionated by using a chromatographic column packed with silica gel using a mixed solvent of ethyl acetate/n-hexane = 1/2 as a developing solvent. The fractionated developing solution was concentrated to obtain 18.6 g of the oily object of the synthesis exemplified compound (5), that is, 5-isobutoxycarbonylamino-4-(2-N,N-dimethylamino ethylthio)-1-hydroxy-N-(3-dodecyloxypropyl)-2-naphthoamide. Yield: 5.9%.

The addition amount of the bleach accelerator releasing type coupler represented by Formula (I) according to the present invention to the photosensitive material is preferably from 1×10^{-7} mol to 1×10^{-1} mol, particularly, from 1×10^{-6} mol to 5×10^{-2} mol per m^2 of the photosensitive material. While the bleach accelerator releasing compound according to the present invention can be added to any of the layers in the photosensitive material, it is preferred to add it to the photosensitive emulsion layer, particularly, a red-sensitive emulsion layer.

Explanation is to be made next for the silver halide color photosensitive material used in the present invention for the emulsion layer in the photosensitive material. Any of silver halides, that is, silver bromide, silver iodobromide, silver chlorobromide, silver chloroiodobromide, silver chloride and silver chloroiodide may be used, but the use of silver iodobromide is particularly preferred. In the case of using silver iodobromide, silver iodide content is usually less than 40 mol%, preferably, less than 20 mol% and more preferably, less than 10 mol%.

The silver halide grains may be so-called regular grains having a regular crystal body such as hexahedron, octahedron, tetradecahedron, etc. or those of irregular crystal forms such as spheres, those having crystal defects such as twine planes or mixed forms thereof. Furthermore, a mixture of grains of various crystal forms may be used.

The silver halide may either be a monodispersed emulsion having a narrow distribution or polydispersed emulsion having a broad distribution.

For the emulsion layer described above, tabular grains with the aspect ratio of 5 or greater may be used.

The crystal structure of the emulsion grains may be uniform or those having a halogen composition different between the inside and the outside or it may be a layered structure. These emulsion grains are disclosed, for example, in British Patent 1,027,146, U.S. Patents 3,505,068, 4,444,877 and JP-A-60-143331. Silver halides of different compositions may be joined by epitaxial junction, or may be joined with other compounds than silver halide such as silver rhodanate or lead oxide.

The emulsion described above may be (A) a surface latent image type whereby latent images are formed mainly on the surface of the grains, or (B) an internal latent image type whereby latent images are formed to the inside of the grains, or (C) a type whereby the latent images are formed both on the surface as well as to the inner side of the grains. Grains in which the inside thereof is chemically sensitized may be used.

Silver halide photographic emulsion usable in the present invention can be produced by properly using a known method. For example, the emulsion can be prepared according to the method as described in Research Disclosure vol. 176, No. 17643 (December 1978), pages 22 to 23, "Emulsion Preparation and Types", vol 187, No. 18716 (November 1979), page 648.

For the preparation of the photographic emulsion in the present invention, it is possible if required to use various types of silver halide solvent, for example, ammonia or potassium rhodanate or thioethers and thion compound as described in U.S. Patent 3,271,157, JP-A-51-12360, JP-A-53-82408, JP-A-53-144319, JP-A-54-100717 or JP-A-54-155828.

As the monodispersed emulsion, typical silver halide grains have the average grains size of not less than about 0.1 m in which at least 95% by weight thereof is within ±40% of the average grain size. Those emulsions with the average grain size from 0.25 to 2 µm in which at least 95% by weight of the number of grains of silver halide grains are within the range of average grain size ±20% can be used.

In the course of forming or physically repening silver halide grains, cadmium salt, zinc salt, lead salt, thalium salt, irridum salt or complex thereof, rhodium salt or complex thereof, iron salt or a complex salt may be present alone or with other of the above mentioned salts.

The emulsion used in the present invention is usually subjected to chemical ripening and spectral sensitization after the physical ripening.

The additives used in such steps are described in Research Disclosure No. 17643 (December, 1978), and No. 18716 (November, 1979) described above and the relevant portions of the literatures are summarized in the Table below.

Known photographic additives usable in the present invention are also described in the two Research Disclosures described in the paragraph above, and the relevant portions are also shown hereinafter in the following Table.

	Type of additives	RD 17643	RD 18716
1.	Chemical sensitizer	P 23	P 648, right column
2.	Sensitivity improver		"
3.	Spectral sensitizer	P 23 - 24	P 648, right column
	Supersensitizer		P 649, right column
4.	Brightening agent	P 24	
5.	Anti-foggant and stabilizer	P 24 - 25	P 649, right column
6.	Light absorber, filter dye UV absorber	P 25 - 26	P 649, right column to 650, left column
7.	Antistaining agent	P 25, right column	P 650, left to right column
8.	Dye image stabilizer	P 25	
9.	Film hardener	P 26	P 651, left column
10.	Binder	P 26	"
11.	Plasticizer, lubricant	P 27	P 650, right column
12.	Coating aid, Surfactant	P 26 - 27	"
13.	Antistatic agent	P 27	"

Although known spectral sensitizers as described above are used for the color photosensitive material in the present invention, it is preferred in the processing method of the present invention to use those compounds and specific compounds represented by Formula (IV) or (V) as described in pages 90 to 110 of the specification in JP-A-63-163853.

In the present invention, various color couplers can be used in addition to the cyan image forming coupler of the Formula (I) and specific examples thereof are described in patent literatures set forth in the Research Disclosure (RD) No. 17643, VII-C to G. As the color forming coupler, those couplers giving three primary colors by subtractive color process (that is, yellow, magenta and cyan) by color development are important, and the following couplers can be used preferably in the present invention in addition to the diffusion resistant 4-equivalent or 2-equivalent coupler specifically described in the patent literatures set forth in Research Disclosure No. 17643, VII-C and D.

Typical examples of the yellow couplers usable herein can include known oxygen atom releasing type yellow coupler or nitrogen atom releasing type yellow coupler. α-Pivaloyl acetoanilide type coupler is excellent in the fastness of color forming dye, particularly, light fastness, whereas α-benzoyl acetoanilide type coupler can provide high color forming density.

The magenta coupler usable in the present invention can include hydrophobic 5-pyrazolone type and pyrazoloazole type coupler having ballast group. Among the 5-pyrazolone type couplers, those substituted at the 3-position with aryl amino group or acyl amino group are preferred in view of the hue and the color forming density of the color forming dye.

The cyan coupler usable in the present invention can further include hydrophobic and diffusion resistant naphthol and phenol type couplers, and 2-equivalent naphthol type coupler of the oxygen atom releasing type can be mentioned as preferred typical examples. Furthermore, those couplers capable of forming cyan dye fast to humidity and temperature are preferably used and typical examples thereof can include phenol type cyan coupler having ethyl or higher alkyl group at the meta-position of the phenol nuclei and 2,5-diacrylamino substituted phenol type coupler, phenol type coupler having phenyl ureido group at the 2-position and diacylamino group at the 5-position as described in U.S. Patent 3,772,002, and 5-amidonaphthol type cyan coupler as described in EP-A-161626.

A coupler in which the color forming dye has an adequate diffusing property may be used together to improve the granular property. For such couplers, specific examples of the magenta coupler are found in U.S. Patent 4,366,237, etc. and specific examples of yellow, magenta or cyan coupler are found in European Patent 96,570, etc.

The dye-forming coupler and the particular coupler described above may form a dimer or a higher polymer. Typical examples of polymerized dye-forming coupler are described in U.S. Patent 3,451,820, etc. Specific examples of polymerized magenta coupler are described in U.S. Patent 4,367,282.

Couplers releasing a photographically useful residual group upon coupling can also be used preferably in the present invention. As DIR coupler releasing development inhibitors, those patented couplers described in RD 17643, VII-F (described above) are useful.

Those couplers releasing a nucleating agent, development accelerator or precursor thereof upon development imagewise can be used for the photosensitive material according to the present invention. Specific examples of such compounds are described in British Patent 2,097,140 and 2,131,188. In addition, it is possible to use DIR redox compound releasing coupler as described in JP-A-60-185950, etc. and couplers releasing dyes restoring color after splitting as described in EP-A-173302.

The coupler used in the present invention can be introduced into the photosensitive material by various known dispersion methods. Examples of high boiling point organic solvents used for the oil in-water droplet dispersion method are described in U.S. Patent 2,322,027. Steps and effect of the latex dispersion method and specific examples of latex for impregnation are described in U.S. Patent 4,199,363, German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

The photosensitive material used in the present invention may also contain hydroquinone derivatives, aminophenol derivatives, amines, gallic acid derivatives, catechol derivatives, ascorbic acid derivatives, non-coloring couplers, sulfonamido phenol derivatives, etc. as an anti-color fogging agent or anti color mixing agent.

Known anti-discoloration agent may be used for the photosensitive material used in the present invention. Typical examples of known anti-discoloration agents can include, for example, hydroquinones, 6-hydroxychromans, 5-hydroxycumarans, spirochromans, p-alkoxyphenols, hindered phenols such as bisphenols, gallic acid derivatives, methylene dioxybenzenes, aminophenols, hindered amines and ether or ester derivatives obtained by silylating or alkylating phenolic hydroxy groups in each of the compounds. Furthermore, metal complexes typically represented by (bissalicylaldoxymato)nickel complex and (bis-N,N-dialkyldithiocarbamato)nickel complex may also be used.

In the photosensitive material according to the present invention the photographic emulsion layer and other layers are coated on a typical flexible support such as plastic films.

The photographic emulsion layer and other hydrophilic colloid layers can be coated by utilizing various known coating methods, for example, dip coating, roller coating, curtain coating and extrusion coating.

The present invention can be applied to various color photosensitive materials. Typical examples thereof can include general-purpose or cinema use color negative films, color reversal film for slide or television use, color paper, color positive film, color reversal paper, etc.

The color developer used for the development of the photosensitive material according to the present invention is an aqueous alkaline solution using an aromatic primary amine color developing agent as the main ingredient. While aminophenol type compound is also useful as the color developing agent, p-phenylene diamine compound is preferably used and typical examples thereof can include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamide ethyl-aniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethyl aniline, as well as sulfate, hydrochloride, phosphate, p-toluene sulfonate, tetraphenyl borate, p-(t octyl) benzene sulfonate thereof.

Usually a salt form of these diamines is more stable and used more preferably than free state.

The aminophenol derivative can include, for example, o-aminophenol, p-aminophenol, 4-amino-2-methylphenol, 2-amino-3-methylphenol and 2-oxy-3-amino-1,4-dimethylbenzene.

In addition, those as described in "Photographic Processing Chemistry" written by L.F.A Mason, published from by Focal Press, pages 226 to 229 (1966), in U.S. Patents 2,193,015, 2,592,364, JP-A-48-64933, etc. may be used. If required, two or more of color developing agents may be used in combination.

The color developer may also contain a pH buffer such as alkali metal carbonate, borate or phosphate; a development inhibitor or anti-foggant such as bromide, iodide, benzoimidazoles, benzothiazoles, and mercapto compounds; a preservative such as hydroxylamine, triethanol amine, compounds described in German Patent Application (OLS) No. 2,622,950, sulfite or hypersulfite; an organic solvent such as diethylene glycol; a development promoter such as benzyl alcohol, polyethylene glycol, quaternary ammonium salt, amines, thiocyanate and, 3,6-thiaoctane-1,8-diol; a dye-forming coupler; competing coupler; a nucleating agent such as sodium boronhydride; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a tackifier; and a chelating agents such as ethylenediamine tetraacetic acid, nitrilotriacetic acid, cyclohexane diamine tetraacetic acid, iminodiacetic acid, N-hydroxymethylethylenediamine triacetic acid, diethylenetriamine pentaacetic acid, triethylenetetramine hexaneacetic acid and aminopolycarboxylic acid represented by the compounds as described in JP-A-58-195845, 1-hydroxyethylinden-1,1′-diphosphonic acid, organic phosphonic acid as described in Research Disclosure No. 18170 (May, 1979), aminophosphonic acid such as aminotris(methylene phosphonic acid), ethylenediamine-N,N,N′,N′ tetramethylene phosphonic acid, etc. phosphono carboxylic acid as described in Research Disclosure No. 18170 (May, 1979).

The color developing agent is used at a concentration of about 0.1 g to about 30 g per one liter of the usual color developer solution, more preferably, at a concentration about from 1 g to about 15 g per one liter of the color developer solution. Further, pH value of the color developer is usually 7 or higher and, most generally, about 9 to 13.

In the present invention, the silver halide color photographic material is applied with color developing treatment as described above after imagewise exposure, and then processed with a processing solution having a bleaching performance.

The processing solution having the bleaching performance means those processing solutions having a performance of oxidizing metal silver resulted from the developing reaction and colloidal silver contained in the photosensitive material thereby converting them into a soluble silver salt such as silver thiosulfate complex or an insoluble silver salt such as silver bromide, and they can include, for example, bleaching solution, or bleach-fixing solution, etc. In the present invention, it is preferred to carry out processing with a processing solution having bleach-fixing performance directly after the processing with the color development.

The bleaching agent used as the processing solution having the bleaching performance in the present invention can include ferric complex salt such as ferricyanate ferric complex salts, citarate ferric salts, etc., and peroxide such as persulfate, hydrogen peroxide, etc. Preferred is aminopolycarboxylic acid ferric complex salt, which is a complex of ferric ions with aminopolycarboxylic acid or the salt thereof.

Typical examples of the aminocarboxylic acids and salts thereof can include, for example:

(1) Diethylenetriamine pentaacetic acid
(2) Pentasodium salt of diethylenetriamine pentaacetic acid
(3) Ethylenediamine-N-(β-oxyethyl)-N,N′,N′-triacetic acid.
(4) Trisodium ethylenediamine-N-(β-oxyethyl)-N,N′,N′ triacetate
(5) Triammonium ethylenediamine-N-(β-oxyethyl)-N,N′,N′-triacetate
(6) 1,2-diaminopropane tetraacetic acid
(7) Disodium 1,2 diaminopropane tetraacetate
(8) Nitrilotriacetic acid
(9) Sodium nitrilotriacetic acid salt
(10) Cyclohexanediamine tetraacetate
(11) Cyclohexanediamine tetraacetic acid disodium salt
(12) N-methyliminodiacetic acid
(13) Iminodiacetic acid
(14) Dihydroxyethyl glycine
(15) Ethylether diamine tetraacetic acid
(16) Glycol ether diamine tetraacetic acid
(17) Ethylenediamine tetrapropionic acid
(18) 1,3 diaminopropane tetraacetic acid and

(19) Ethylenediamine tetra-acetic acid.

This invention is in no way limited to these exemplified compounds.

Among the compounds described above, (1), (2), (6), (7), (10), (11), (16), (18) are particularly preferred.

The aminocarboxylic acid ferric complex salt may be used in the form of a complex salt, or ferric ion complex salt may be formed in a solution using ferric salt, for example, ferric sulfate, ferric chloride, ferric sulfate, ammonium ferric sulfate and ferric phosphate with aminocarboxylic acid. In the case of using aminocarboxylic acid ferric complex salt as a complex salt, the complex salt may be used alone or as a mixture of two or more of them. While on the other hand, in the case of forming a complex salt in a solution using a ferric salt and an aminocarboxylic acid, one or more of the ferric salts may be used. Furthermore, one or more of aminocarboxylic acids may be used. Further, in any case, aminopolycarboxylic acid may be used in excess amounts for forming the ferric ion complex salts.

Further, at least one of aminopolycarboxylic acid Fe (III) complex salt described above, except for (19), and ethylenediamine tetraacetic acid Fe (III) complex salt may be used in combination.

The processing solution having the bleaching function containing the ferric complex salt described above may contain metal ion complex salts such as of cobalt, nickel and copper other than iron ions.

The amount of the bleaching agent per one liter of the processing solution having the bleaching performance according to the present invention is from 0.1 mol to 1 mol, preferably, from 0.2 mol to 0.5 mol. Further, the pH value of the bleaching solution is preferably from 4.0 to 8.0 and, particularly, from 5.0 to 7.5.

The processing bath having the bleaching performance constituting the present invention can contain, in addition to the bleaching agent and the compound as described above, a re-halogenating agent such as bromide, (for example, potassium bromide, sodium bromide, ammonium bromide) or chloride, (for example, potassium chloride, sodium chloride and ammonium chloride). In addition, those additives known to be used for tin bleach-fixing solution such as one or more inorganic acid, organic acids and salts thereof having pH buffering performance can be added, for example, nitrate (such as sodium nitrate and ammonium nitrate), boric acid, borax, sodium metaborate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorous acid, phosphoric acid, sodium phosphate, citric acid, sodium citrate and tartaric acid.

In the present invention, the fixing bath subsquent to the bleaching bath or a processing bath having bleach-fixing performance can be incorporated with those compounds known as fixing agents such as thiosulfate, (for example, sodium thiosulfate, ammonium thiosulfate, ammonium sodium thiosulfate and potassium thiosulfate), thiocyanate (such as ammonium thiocyanate and potassium thiocyanate), thiourea and thioether. The addition amount of these fixing agents is preferably less than 3 mol and, particularly preferably less than 2 mol per one liter of the processing solution having the fixing performance or the processing solution having the bleach-fixing performance.

The processing solution having the bleach-fixing performance in the present invention can be incorporated with so-called sulfite ion releasing compounds such as sulfite, (for example, sodium sulfite and ammonium sulfite), hydrogensulfite or aldehyde and hypersulfite addition product (for example, carbonylbisulfite). Furthermore, it is possible to incorporate aminopolycarboxylic acid salts as shown from (1) to (19), or organic phosphonic acid compounds such as ethylenediamine tetrakismethylenephosphonic acid, diethylenetriamine pentakismethylenephosphonic acid, 1,3-diaminopropane tetrakis methylenephosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, 1-hydroxyethylidene-1,1′-diphosphonic acid, etc.

In the present invention, at least one bleaching accelerator selected from compounds having mercapto group or disulfide bond, isothiourea derivatives and thiazolidine derivatives may be incorporated in the processing solution having the bleaching function for conducting the processing. The amount of such compounds per one liter of the processing solution having the bleach fixing performance is preferably from 1×10^{-5} to 1×10^{-1} mol and, more preferably, from 1×10^{-4} to 5×10^{-2}.

The bleaching accelerator incorporated in the processing solution having the bleaching performance in the present invention is selected from the compounds having mercapto group or disulfide bond, thiazolidine derivative, thiourea derivative and isothio derivatives, so long as they are effective in bleaching acceleration. Those compounds and specific examples are preferably described in the specification of JP-A-63-163853.

For adding the compound into the processing solution, it is generally preferred to previously dissolve in water, alkaline organic acid organic solvent, etc. If the compound is added in the form of powder as it is directly to the processing bath having the bleaching function, this causes no undesired effect at all for the bleaching acceleration.

Furthermore, the bleaching accelerator can be incorporated into the photosensitive material in the present invention. In this case, the bleaching accelerator can be incorporated into any one of the blue-sensitive, green-sensitive and red-sensitive emulsion layers, or a gelatin layer at the uppermost, intermediate or the lowermost layer.

The processing bath having the bleach-fixing performance according to the present invention may be a step including one vessel. Alternatively, it may be constituted as a step including two or more vessels in which replenishing solution is supplied to the group of vessels in a multi-stage countercurrent system. Furthermore, the processing solutions in the group of the vessels may be circulated to form a uniform processing solution as the whole and the replenishing solution may be supplied to one of the vessels of the group.

The silver halide color photosensitive material according to the present invention is usually applied with desilvering processing such as fixing or bleach-fixing and, thereafter, subjected to a water washing and/or stabilizing step.

The amount of the washing water in the water washing step can be set within a wide range depending on the characteristics of the photosensitive material, for example, material used such as coupler, application use and, further, temperature of the washing water, number of the water washing vessels (number of steps), replenishing system such as countercurrent or normal current type etc, as well as like other various conditions. Among them, the relationship between the number of water washing vessels and the amount of water in the multi-stage countercurrent system can be determined by the method as described in "Journal of the Society of Motion Picture and Television Engineers", Vol. 64, pages 248 to 253 (May, 1955).

According to the multi-stage countercurrent system described in the literature above, although the amount of washing water can remarkably be decreased, this results in problems such as bacteria propagation due to the increase in the water staying time within the vessel causing deposition of suspending matters to the photosensitive material. In the processing of the color photosensitive material according to the present invention, a method of reducing calcium and magnesium as described in JP-A-62-288838 can be used extremely effectively as the countermeasure for such problem. Furthermore, isothiazolone compound or cyabendazoles, chlorine type fungicides such as chlorinated sodium isocyanurate or other benzotriazole, etc. as described in JP-A-57-8542, as well as bacteriocide described in "Chemistry of Bacteriocide and Fungicide" written by Hiroshi Horiuchi, "Microorganism Fungicide, Bacteriocide and Fungicide Technology" edited by Eisei Gijutsukai, "Bacteria and Fungi Control Encyclopedia" edited by Nippon Bacteria and Fungi Controlling Society can also be used.

pH value for the washing water in the processing of the photosensitive material according to the present invention is from 4 to 9, preferably, 5 to 8. The temperature and the time for water washing can also be set variously depending on the characteristics and the application uses of the photosensitive material and it is generally selected within a range from 20 sec to 10 min at 15 to 45 °C, preferably, from 30 sec to 5 min at 25 to 40 °C.

Furthermore, the photosensitive material according to the invention can be processed directly with a stabilizing solution instead of water washing. In such a stabilizing processing, all of known methods can be used as described in JP-A-57-8543, JP-A-58-14834, JP-A-59-184343, JP-A-60-220345, JP-A-60-238832, JP-A-60-239784, JP-A-60-239749, JP-A-61-4054, JP-A-61-118749, etc. Particularly, stabilizing baths containing 1-hydroxyethylidene-1,1-diphosphonic acid, 5-chloro-2-methyl-4-isothiazolin-3-one, bismuth compound, ammonium compound, etc. can preferably be used.

In addition, there is a case of applying a further stabilizing processing subsequent to the water washing processing. A stabilizing bath containing formalin and surface active agent used as the final bath for the camera film type color photosensitive material can be mentioned as an Example.

The following examples are intended to illustrate the present invention but not to limit it in any manner.

EXAMPLE 1

On a cellulose triacetate film support applied with primer coating, Specimen 101 which is a multilayered color photosensitive material comprising each of the layers of the composition shown below was prepared. (Composition of the photosensitive layer)

The coating amount was shown, for the silver-halide and colloidal silver by the amount of silver represented by g/m^2 unit, for the coupler, additive and gelatin, by the amount represented by g/m^2 unit and, for the sensitizing dye, by the mol number per one mol of silver halide in one identical layer.

First Layer (Anti-halation layer)

Black colloidal silver	0.2
Gelatin	1.3
ExM-8	0.06
UV-1	0.1
UV-2	0.2
Solv-1	0.01
Solv-2	0.01

Second Layer (Intermediate layer)

Silver halide fine grains (average grain size 0.07 μ)	0.10
Gelatin	1.5
UV-1	0.06
UV-2	0.03
ExC-2	0.02
ExF-1	0.004
Solv-1	0.1
Solv-2	0.09

Third Layer (First red-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 2 mol%, internal high AgI type, diameter as sphere 0.3 μ, variation coefficient for the spherical diameter 29%, regular twine crystal mixed grain, diameter/thickness ratio 2.5)
0.4 amount of silver coating

Gelatin	0.6
ExS-1	1.0×10^{-4}
ExS-2	3.0×10^{-4}
ExS-3	1.0×10^{-5}
ExC-3	0.06
ExC-4	0.06
ExC-7	0.04
ExC-2	0.03
Solv-1	0.03
Solv-2	0.012

Fourth Layer (Second red-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 5 mol%, internal high AgI type, diameter as sphere 0.7 μ, variation coefficient for the spherical diameter 25%, regular twine crystal mixed grain, diameter/thickness ratio 4)
0.7 amount of silver coating

Gelatin	0.5
ExS-1	1.0×10^{-4}
ExS-2	3.0×10^{-4}
ExS-3	1.0×10^{-5}
ExC-3	0.24
ExC-4	0.24
ExC-7	0.04

ExC-2	0.04
Solv-1	0.15
Solv-3	0.02

Fifth layer (Third red-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 10 mol%, internal high AgI type, diameter as sphere 0.8 μ, variation coefficient for the spherical diameter 16%, regular twine crystal mixed grain, diameter/thickness ratio 1.3)

1.0 amount of silver coating

Gelatin	1.0
ExS-1	1.0×10^{-4}
ExS-2	3.0×10^{-4}
ExS-3	1.0×10^{-5}
ExC-6	0.13
Solv-1	0.01
Solv-3	0.05

Sixth Layer (Intermediate layer)

Gelatin	1.0
Cpd-1	0.03
Solv-1	0.05

Seventh Layer (First green-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 2 mol%, internal high AgI type, diameter as sphere 0.3 μ, variation coefficient for the spherical diameter 28%, regular twine crystal mixed grain, diameter/thickness ratio 2.5)

0.30 amount of silver coating

ExS-4	5.0×10^{-4}
ExS-6	0.3×10^{-4}
ExS-5	2.0×10^{-4}
Gelatin	1.0
ExM-9	0.2
ExY-14	0.03
ExM-8	0.03
Solv-1	0.5

Eighth Layer (Second green-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 4 mol%, internal high AgI type, diameter as sphere 0.6 μ, variation coefficient for the spherical diameter 38%, regular twine crystal mixed grain, diameter/thickness ratio 4)

0.4 amount of silver coating

Gelatin	0.5
ExS-4	5.0×10^{-4}
ExS-5	2.0×10^{-4}
ExS-6	0.3×10^{-4}
ExM-9	0.25
ExM-8	0.03

ExM-10	0.015
ExY-14	0.01
Solv-1	0.2

Ninth Layer (Third green-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 6 mol%, internal high AgI type, diameter as sphere 1.0 μ, variation coefficient for the spherical diameter 80%, regular twine crystal mixed grain, diameter/thickness ratio 1.2)	0.85 amount of silver coating
Gelatin	1.0
ExS-7	3.5×10^{-4}
ExS-8	1.4×10^{-4}
ExM-11	0.1
ExM-12	0.03
ExM-13	0.20
ExM-8	0.02
ExY-14	0.02
Solv-1	0.20
Solv-2	0.05

Tenth Layer (Yellow filter layer)

Gelatin	1.2
Yellow colloidal silver	0.08
Cpd-2	0.1
Solv-1	0.3

Eleventh Layer (First blue-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 4 mol%, internal high AgI type, diameter as sphere 0.5 μ, variation coefficient for the spherical diameter 15%, octahedron grain)	0.40 amount of silver coating
Gelatin	1.0
ExS-9	2×10^{-4}
ExY-16	0.9
ExY-14	0.07
Solv-1	0.20

Twelfth Layer (Second blue sensitive emulsion layer)

Silver iodobromide emulsion (AgI 10 mol%, internal high AgI type, diameter as sphere 1.3 μ, variation coefficient for the spherical diameter 25%, regular twine crystal mixed grain, diameter/thickness ratio 4.5)	0.50 amount of silver coating
Gelatin	0.6
ExS-9	1×10^{-4}
ExY-16	0.25
Solv-1	0.07

Thirteenth Layer (First protective layer)

Gelatin	0.8
UV-1	0.1
UV-2	0.2
Solv-1	0.01
Solv-1	0.01

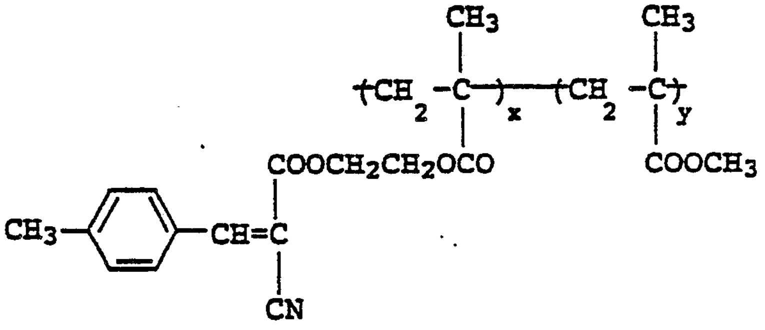
Fourteenth Layer (Second protective layer)

Silver bromide fine grains (average grain size 0.07 μ)	0.5
Gelatin	0.45
Polymethylmethacrylate (diameter1.5 μ)	0.2
H-1	0.4
Cpd-3	0.5
Cpd-4	0.5

In addition to the ingredients described above, a surface active agent was added as a coating aid to each of the layers. The specimen prepared as described above is referred to as Specimen 101.

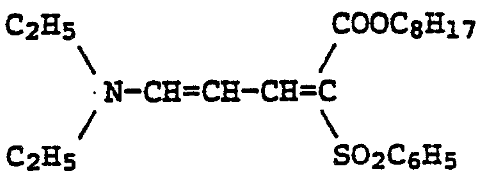
The chemical structural formula or chemical names of the compounds used in the present invention are shown below, however, the present invention is not to be construed as being limited thereto.

UV-1



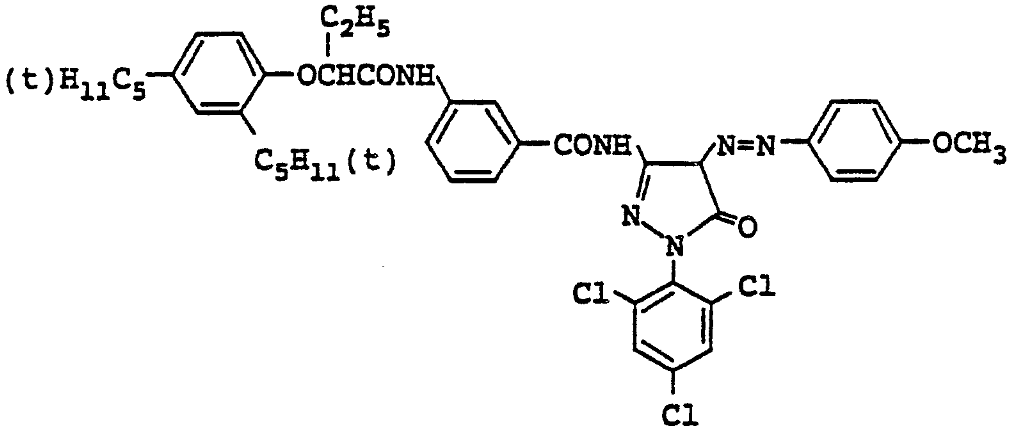
x/y=7/3 (weight ratio)

UV-2

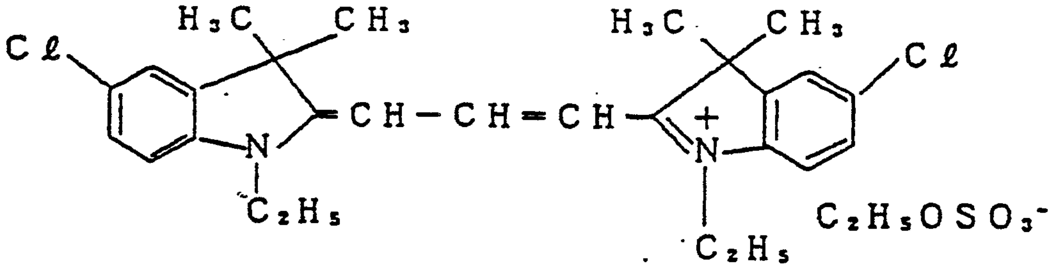


Solv-1 Tricresyl phosphate
Solv-2 Dibutyl phthalate
Solv-3 Bis(2-ethylhexyl)phthalate

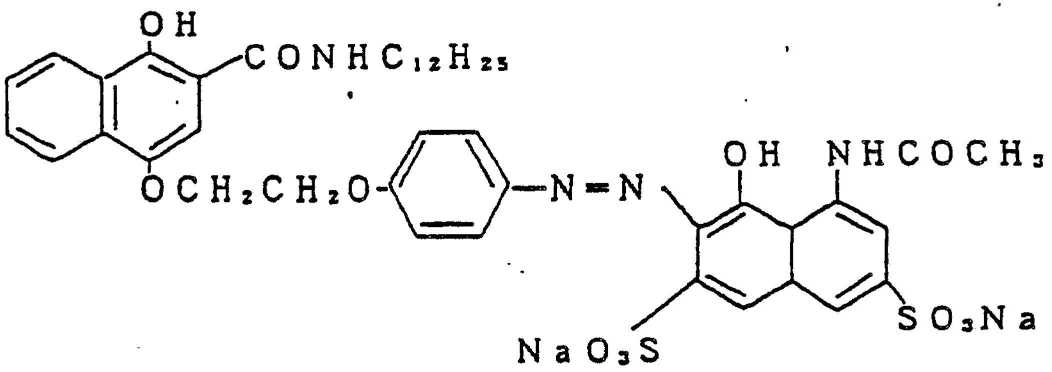
ExM-8


C2H5
(t)H11C5
OCHCONH
C5H11(t)
CONH
N=N
OCH3
N
N
O
Cl
Cl
Cl

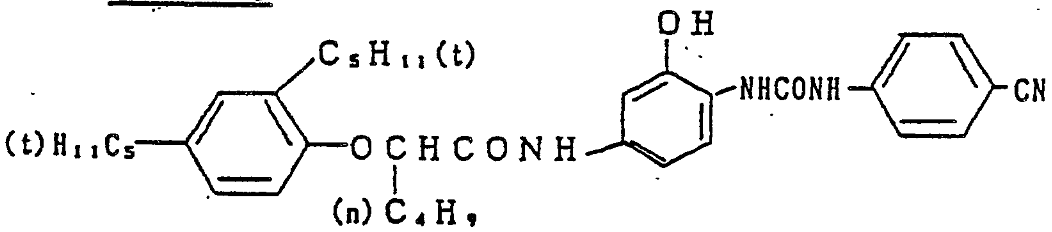
ExF-1


Cℓ
H3C
CH3
CH−CH=CH
N
C2H5
H3C
CH3
Cℓ
+
N
C2H5
C2H5OSO3⁻

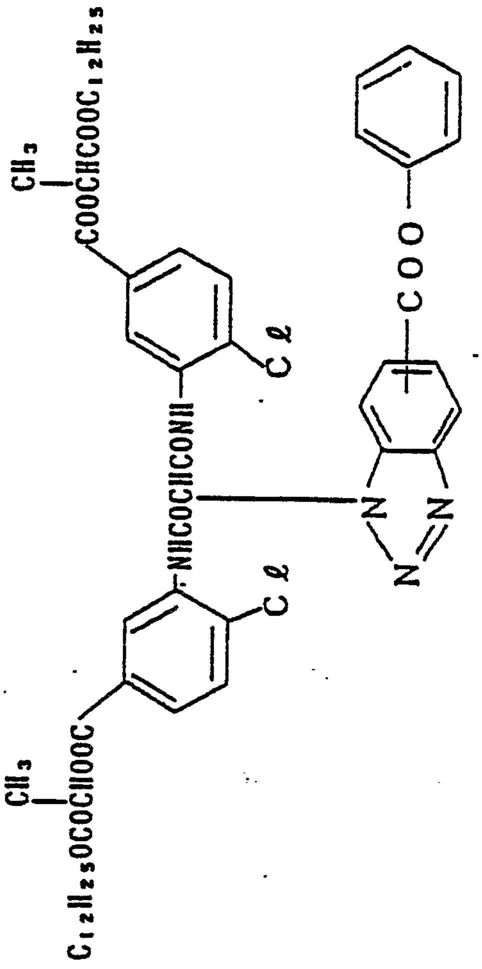
ExC-2


OH
CONHC₁₂H₂₅
OCH₂CH₂O
N=N
OH
NHCOCH₃
SO₃Na
NaO₃S

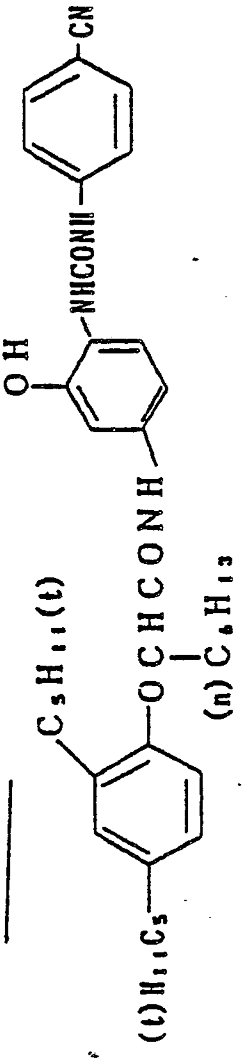
ExC-3


C₅H₁₁(t)
(t)H₁₁C₅
OCHCONH
(n)C₄H₉
OH
NHCONH
CN

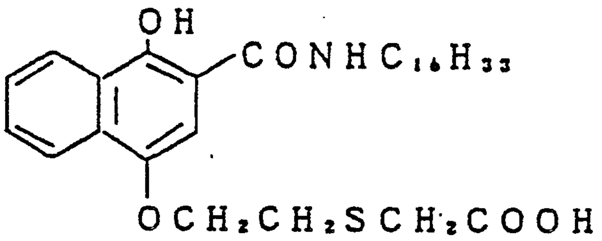
ExY-14



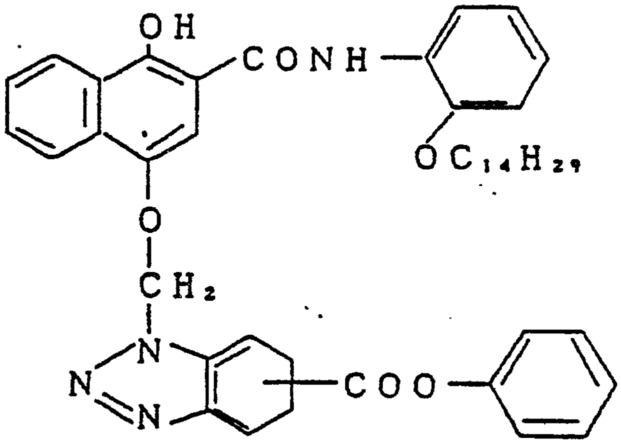
ExC−4



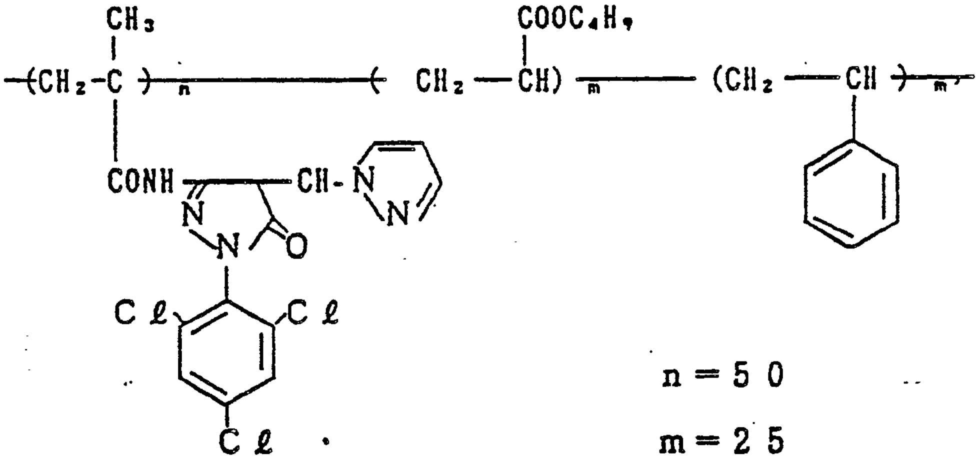
ExC-6


OH
CONHC16H33
OCH2CH2SCH2COOH

ExC-7


OH
CONH
OC14H29
O
CH2
N
N
N
COO

ExM-9



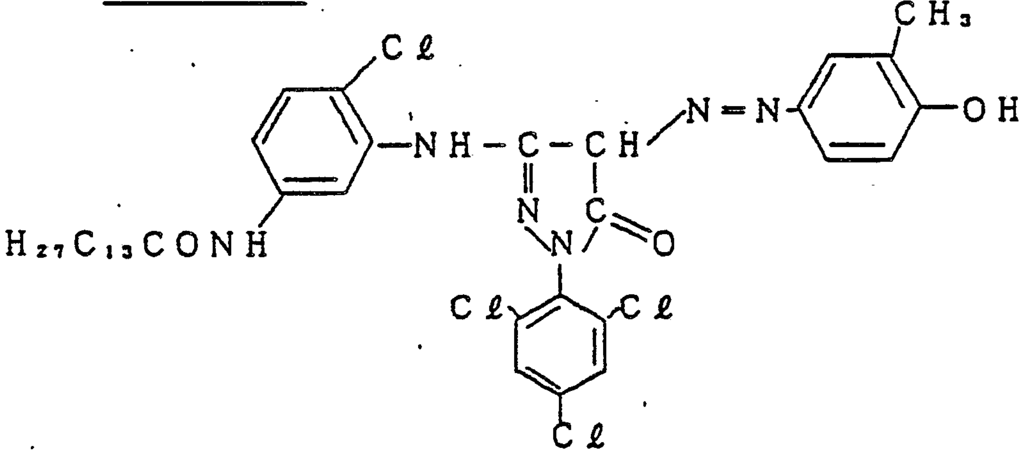
n = 50

m = 25

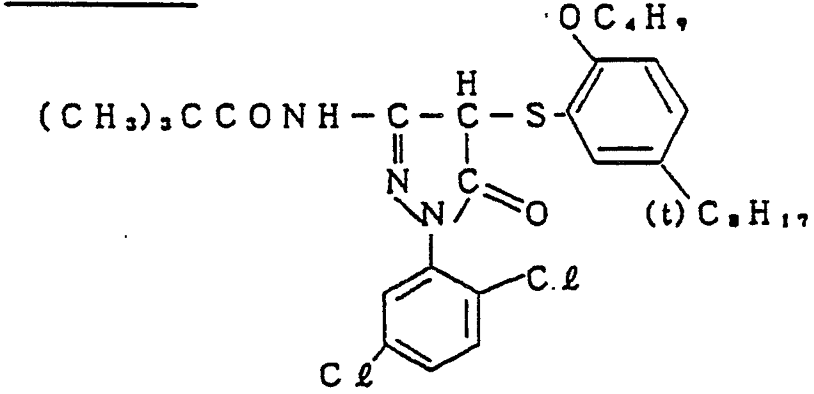
m' = 25

mol.wt. about 20,000

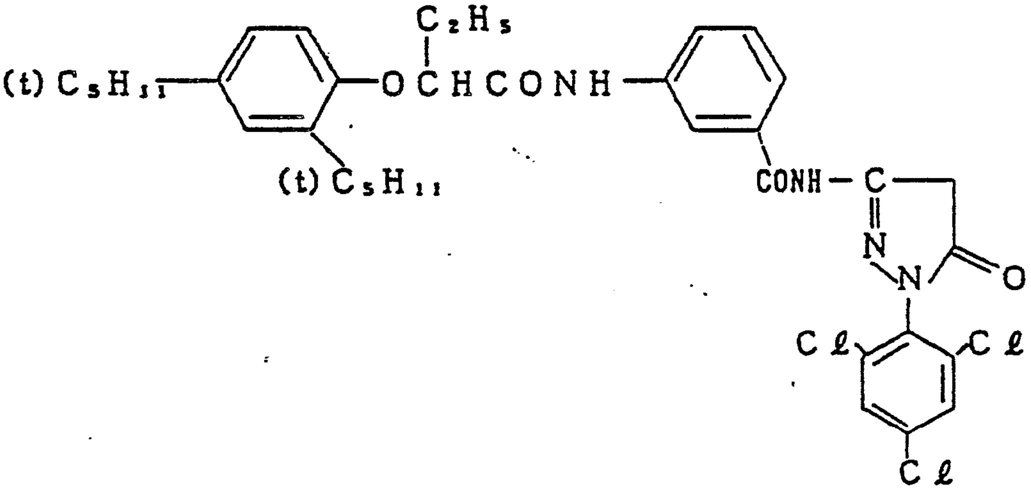
ExM-10



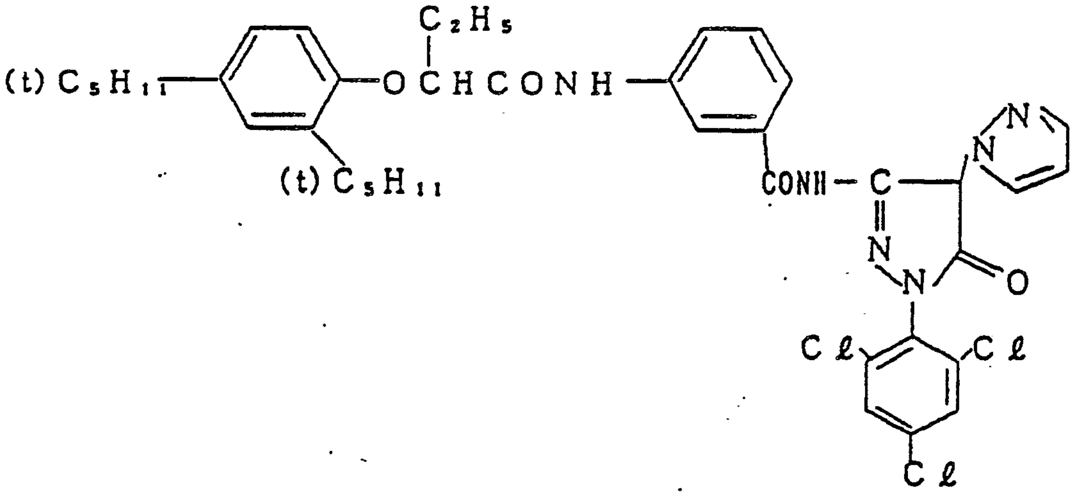
ExM-11



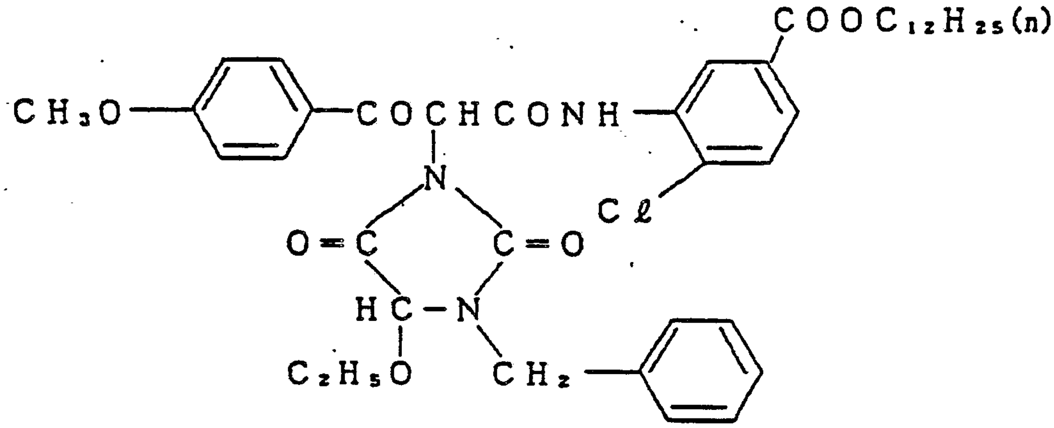
ExM-12



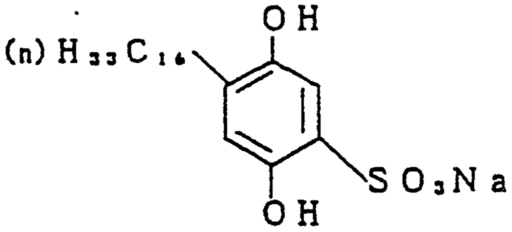
ExM-13



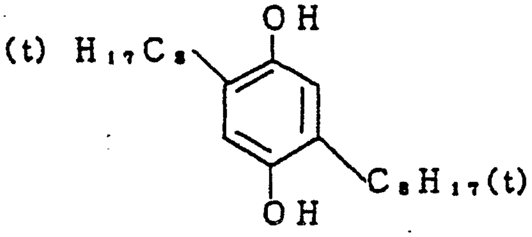
ExY-16



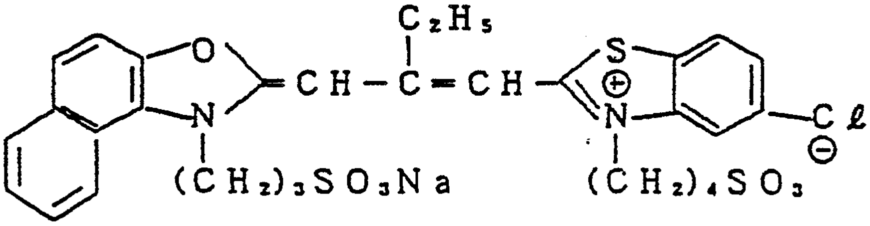
Cpd-1



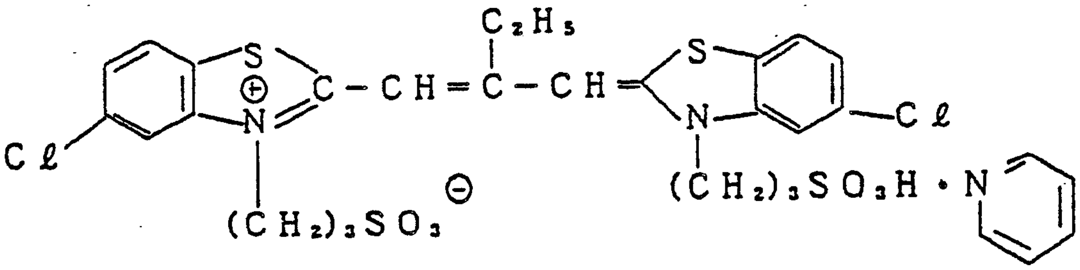
Cpd-2



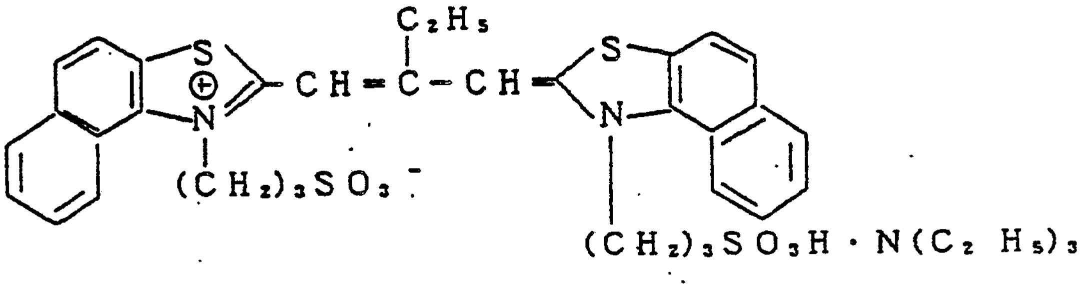
ExS-1



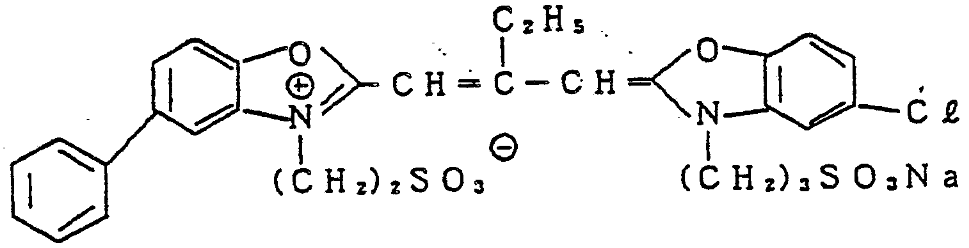
ExS-2



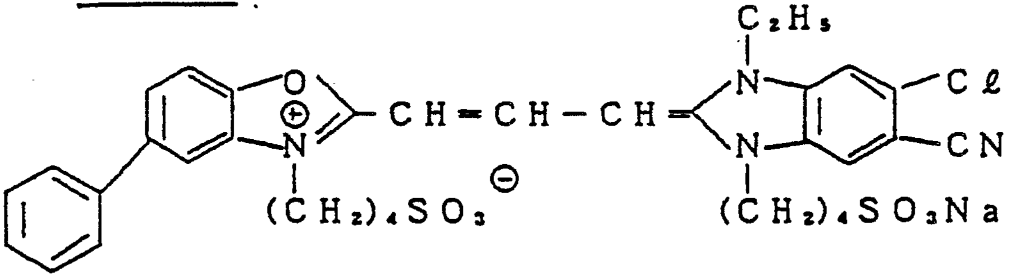
ExS-3



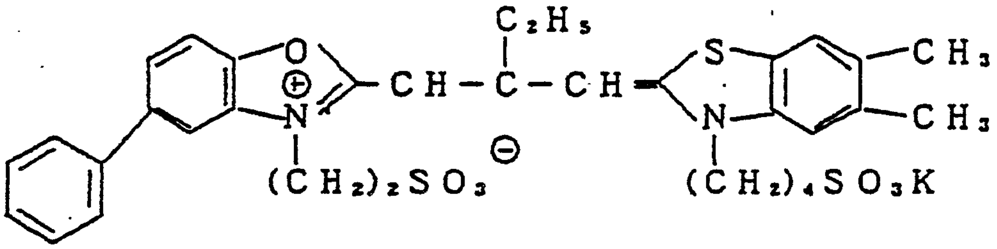
ExS-4



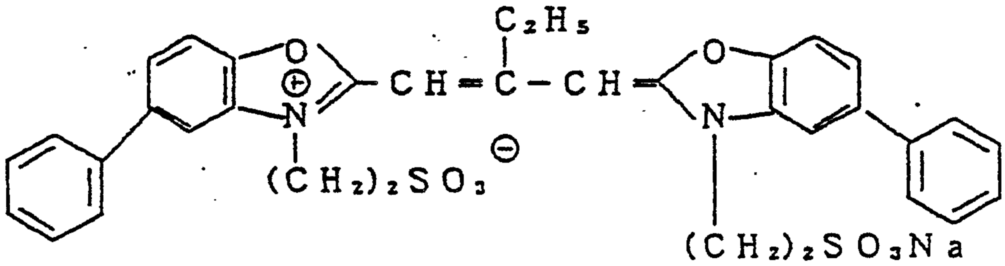
ExS－5



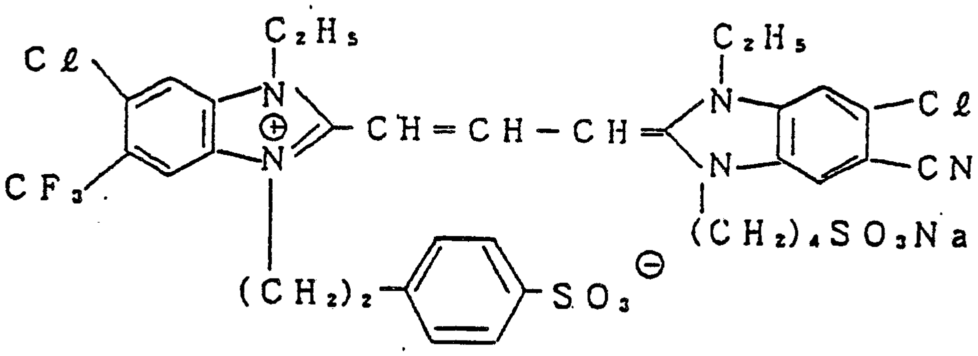
ExS－6



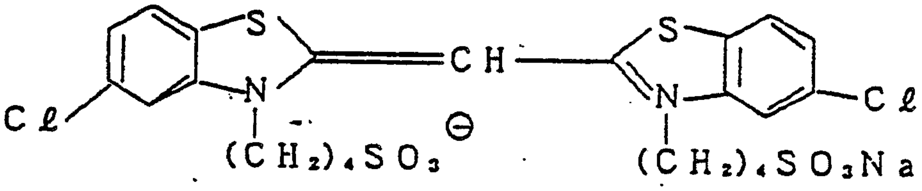
ExS－7



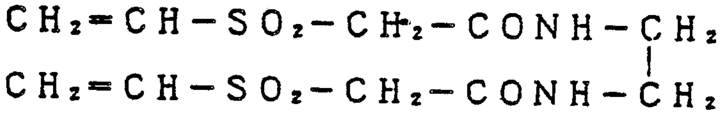
ExS-8



ExS-9

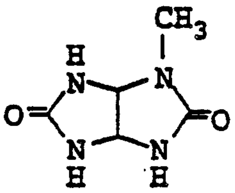


H-1

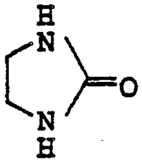


$$\begin{array}{l} \mathrm{CH_2=CH-SO_2-CH_2-CONH-CH_2} \\ \hphantom{\mathrm{CH_2=CH-SO_2-CH_2-CONH-}}| \\ \mathrm{CH_2=CH-SO_2-CH_2-CONH-CH_2} \end{array}$$

Cpd-3



Cpd-4



Specimens 102 to 110

Specimens 102 to 110 were prepared in the same manner as in Specimen 101 by using comparative compounds A, B and C, the compound of the present invention each in an equal molar amount instead of the coupler EXC-6 added to the fifth layer in Specimen 101.

After cutting the obtained Specimens each 101 to 110 into 35 mm width, a standard object was photographed and a running test was carried out respectively through the following processing steps (I) to (III). After the end of the running, each of Specimens 101 to 110 was exposed with 20 CMS by white light, each of the running solutions was passed and the practical allowable range of residual silver amount measured by fluorescent X-ray was less than 30 mg/m^2.

Measurement for Dmin and measurement for sensitivity were also conducted.

Furthermore, the specimens passed through the processing (III) were stored under 80°C, 70% HR atmosphere for 30 days in a dark place to examine the color image fastness.

The result is shown in Table 1.

Processing Operation (I) (Temperature 38°C)

	Process (I)	
Step	Time	Replenish amount*
Color development	3 min. 15 sec.	15 ml
Bleaching	3 min. 00 sec.	5 ml
Fixing	4 min. 00 sec.	30 ml
Stabilizing (1)	30 sec.	-
Stabilizing (2)	30 sec.	-
Stabilizing (3)	30 sec.	30 ml
Drying	1 min. 30 sec. 50°C	-

*: Per 35 mm width, 1 m length of photosensitive material

In the above processing step, the stabilization steps (1), (2) and (3) were conducted as the countercurrent system of (3) → (2) → (1). The amount of the fixing solution carried to the water washing vessel was 2 ml per 1 m.

(Color development solution)

	Mother liquid (g)	Replenish solution (g)
Diethylenetriamine pentaacetic acid	1.0	2.0
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0	3.3
Sodium sulfite	4.0	5.0
Potassium carbonate	30.0	38.0
Potassium bromide	1.4	-
Potassium iodide	1.3 mg	-
Hydroxylamine	2.4	3.2
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5	7.2
Made up with water to	1 liter	1 liter
pH	10.00	10.05

(Bleaching solution)

	Mother liquid (g)	Replenish solution (g)
Ammonium ethylenediamine tetraacetato ferrate	50	60
Ammonium 1,3-diaminopropane tetraacetato ferrate	60	72
Aqueous ammonia	7 ml	5 ml
Ammonium nitrate	10.0	12.0
Ammonium bromide	150	170

Made up with water to	1 liter	1 liter
pH	6.0	5.8

(Fixing solution)

	Mother liquid (g)	Replenish solution (g)
Disodium ethylenediamine tetraacetate	1.0	1.2
Sodium sulfite	4.0	5.0
Sodium hydrogen sulfite	4.6	5.8
Aqueous ammonium thiosulfate solution (70%)	175 ml	200 ml
Made up with water to	1 liter	1 liter
pH	6.6	6.6

(Stabilizing solution)

	Mother liquid (g)	Replenish solution (g)
Formalin (37% w/v)	2.0 ml	3.0 ml
Polyoxyethylene-p-monononyl-phenyl ether (average polymerization degree 10)	0.3	0.45
5-Chloro-2-methyl-4-isothiazolin-3-one	0.03	0.45
Made up with water to	1 liter	1 liter

Processing Operation (II) (Temperature 38°C)

Step	Process (II) Time	Process (II) Replenish amount*
Color development	3 min. 15 sec.	15 ml
Bleaching	1 min. 00 sec.	10 ml
Bleach-fixing	3 min. 15 sec.	15 ml
Water washing (1)	40 sec.	-
Water washing (2)	1 min. 00 sec.	12 ml
Stabilizing	20 sec.	15 ml
Drying	1 min. 15 sec. 60°C	-

*: Per 35 mm width, 1 m length of photosensitive material

In the above processing step, the water washing (1) and (2) were conducted as the countercurrent system of (2) → (1). Composition for each of the processing solutions is described below.

(Color developing solution)

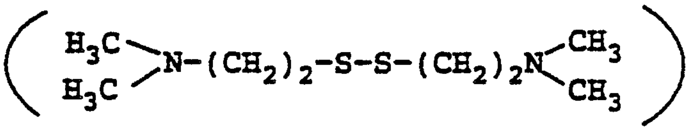
	Mother liquid (g)	Replenish solution (g)
Diethylenetriamine pentaacetate	1.0	1.1
1-Hydroxyethylidene-1,1-diphosphonate	2.0	2.2
Sodium sulfite	4.0	4.9
Potassium carbonate	30.0	42.0
Potassium bromide	1.6	-

Potassium iodide	2.0 mg	-
Hydroxylamine	2.4	3.6
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	5.0	7.3
Made up with water to	1 liter	1 liter
pH	10.00	10.05

Bleaching solution:

In common with the mother liquid and replenishing solution

Ammonium ethylenediamine tetraacetato ferrate	120.0 g
Disodium ethylenediamine tetraacetate	10.0 g
Ammonium nitrate	10.0 g
Ammonium bromide	100.0 g
Bleaching accelerator	1×10^{-3} mol



$$\left(\begin{matrix}H_3C\\H_3C\end{matrix}>N-(CH_2)_2-S-S-(CH_2)_2N<\begin{matrix}CH_3\\CH_3\end{matrix}\right)$$

With an aqueous ammonia	pH 6.3
Made up with water to	1.0 liter

Bleach-Fixing solution:

In common with the mother liquid and replenishing solution

Ammonium ethylenediamine tetraacetato ferrate	50.0 g
Disodium ethylenediamine tetraacetate	5.0 g
Sodium sulfite	12.0 g
Aqueous ammonium thiosulfate (70%)	240 ml
With an aqueous ammonia	pH 7.3
Made up with water to	1.0 liter

Washing water

Tap water passed through a column packed with Na type strongly acidic cationic exchange resin (Diaion SK-1B) manufactured by Mitsubishi Chemical Industries Ltd., to adjust to the water quality: 2 mg/liter of calcium and 1.2 ml/liter of magnesium was used as the water for washing.

Stabilizing solution

Same as in the processing step (I).

Processing Operation (III) (Temperature 38°C)

Step	Processing Time	Tank Volume	Supplement amount*
Color development	3 min. 15 sec.	8 liters	15 ml
Bleach-fixing	2 min. 30 sec.	8 liters	25 ml
Water washing (1)	20 sec.	4 liters	-
Water washing (2)	20 sec.	4 liters	3-stage counter-current system
Water washing (3)	20 sec.	4 liters	10 ml
Stabilization	20 sec.	4 liters	10 ml

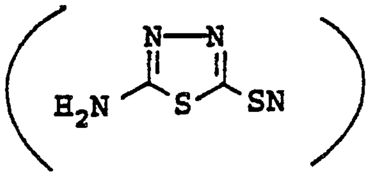
*: Per 35 mm width, 1 m length of photosensitive material

(Color development solution)

	Mother liquid (g)	Replenish solution (g)
Diethylenetriamine pentaacetate	1.0	1.2
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0	2.4
Sodium sulfite	2.0	4.8
Potassium carbonate	35.0	45.0
Potassium bromide	1.6	-
Potassium iodide	2.0 mg	-
Hydroxyamine	2.0	3.6
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	5.0	7.5
Made up with water to	1 liter	1 liter
pH (using potassium hydroxide)	10.20	10.35

(Bleach-fixing solution)

	Mother liquid (g)	Replenish solution (g)
Ammonium ethylenediamine tetraacetato ferrate	40	45
Ammonium diethylenetriamine pentaacetato ferrate	40	45
Disodium ethylenediamine tetraacetate	10	10
Sodium sulfite	15	20
Aqueous ammonium thiosulfate solution (70% w/v)	240	270
Bleaching accelerator	0.1	0.15



Aqueous ammonia (26%)	14 ml	14 ml
Made up with water to	1 liter	1 liter
pH	6.7	6.5

Washing water

The following three types of water was used.

(1) Tap Water

Calcium	26 mg/liter
Magnesium	9 mg/liter
pH	7.2

(2) Ion exchange processed water

The tap water was processed by using a strongly acidic cationic exchange resin (Na type) manufactured by Mitsubishi Chemical Industries Ltd. to adjust the water quality as described below. Calcium 1.1 mg/liter

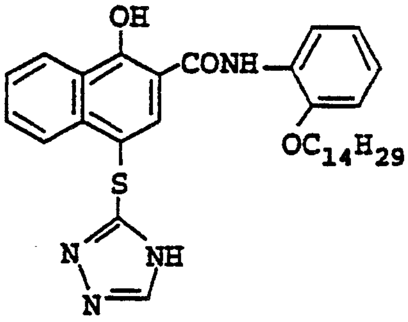
Magnesium	0.5 mg/liter
pH	6.6

(3) Tap water added with chelate agent

Disodium ethylenediamine tetraacetate was added by 500 mg/liter to the tap water described above. pH 6.8

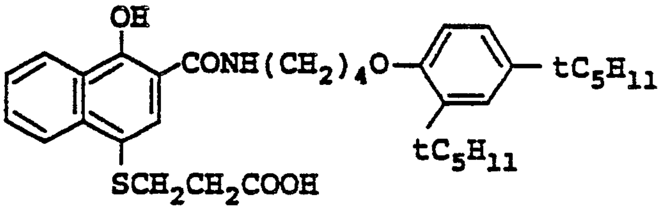
Processing was carried out by using the steps and processing solutions as described above.

Comparative Coupler A



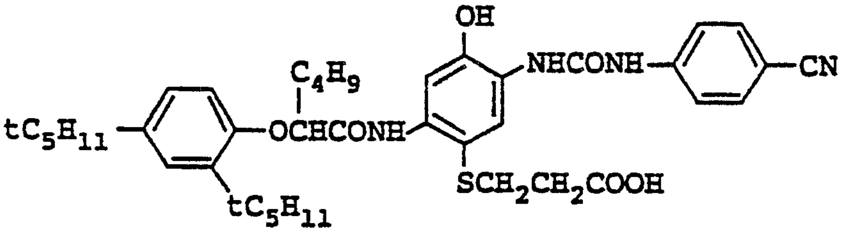
Compound described in Research Disclosure No. 11449 (1973)

Comparative Coupler B



Compound described in JP-A-61-201247

Comparative Coupler C



Compound described in JP-A-61-201247

Specimens 101 to 110 were processed in the same manner as in the processing step (III) except for changing the replenishing amount in the water washing step from 10 ml to 125 ml (referred to as Processing step (IV)).

Dmin of the specimen (magenta) after processing was measured and compared with that in the processing step (III).

As a result, Dmin was reduced by 0.05 for the Specimen 104, but it was substantially the same for other specimens.

From the result, it can be seen that although the comparative coupler C is excellent in the dark discoloration property, increase in Dmin is large when the amount of replenishing washing water is low.

Table 1

Specimen No.	Coupler in sixth layer	Silver residual amount (mg/m^2) Processing (I)	Processing (II)	Processing (III)	Dark discoloration of cyan color image*	Dmin (magenta)**	Sensitivity***
101 (Comparison)	EXC-6	95	120	140	0.18	0.12	±0 (control)
102 (")	A	14	41	69	0.16	0.12	+0.01
103 (")	B	9	23	30	0.18	0.13	-0.05
104 (")	C	18	49	82	0.02	0.21	-0.12
105 (Invention)	(3)	8	21	29	0.02	0.12	+0.01
106 (")	(5)	7	20	26	0.02	0.12	+0.01
107 (")	(6)	9	18	20	0.01	0.12	±0
108 (")	(8)	6	18	23	0.03	0.13	+0.02
109 (")	(18)	9	20	26	0.02	0.12	-0.01
110 (")	(19)	8	19	24	0.02	0.12	+0.02

* Reduction of density from the initial density 1.0 after storing for 30 days at 80°C and 70% RH

** Value obtained by subtracting the film base density

*** Represented by LogE for the difference with respect to the value ±0 of Specimen 101

As apparent from the result of Table 1, it can be seen that the coupler of the present invention when used shows remarkable effect in the reduction of the residual silver amount and the fastness of cyan color image, with no side effect such as increase in Dmin and has sufficient sensitivity as well.

Example 2

The same running processing was carried out as in Example 1 while changing the pH value of the bleach-fixing bath used in the processing step (III) to 6.0, 5.7, 5.5. Then, residual silver amount and the density of the cyan dye image were measured through Specimens 101 to 110 subjected to wedge exposure.

Then, after processing the processing agent strips with the bleaching solution in the processing step (I) for 4 min thereby sufficiently recovering the concentration, the concentration was measured.

The result is shown in Table 2.

Table 2

Specimen	pH 6.7		pH 6.0		pH 5.7		pH 5.5	
	Silver residual amount	Reduction in the cyan concentration	Silver residual amount	Reduction in the cyan concentration	Silver residual amount	Reduction in the cyan concentration	Silver residual amount	Reduction in the cyan concentration*
101 (Comparison)	140	0.01	97	0.05	66	0.20	40	0.20
102 (")	69	0.01	43	0.06	28	0.21	10	0.21
103 (")	30	0.01	10	0.04	7	0.18	4	0.19
104 (")	82	0.01	56	0.01	33	0.02	12	0.03
105 (Invention)	29	0.01	10	0.01	6	0.01	3	0.02
106 (")	26	±0	11	0.01	6	0.02	2	0.02
107 (")	20	±0	11	0.01	6	0.02	1	0.02
108 (")	23	±0	12	0.01	5	0.02	2	0.02
109 (")	26	±0	10	±0	6	0.02	3	0.02
110 (")	24	0.01	12	0.01	6	0.01	3	0.02

* Difference in the concentration between before and after immersion in the bleaching bath in the processing step (I) (represented by the reduction from the concentration 1.0 after immersion in the bleaching bath)

It can be seen that the use of the coupler according to the present invention can provide a sufficient cyan concentration even passed through a bleach-fixing bath at low pH effective to the improvement of the desilvering rate, and it can satisfy both the improvement in the desilvering property when using bleach-fixing bath at low pH and the stability of the cyan dye image (resistivity to the reduction in color restoreability).

EXAMPLE 3

On a cellulose triacetate film support applied with primer coating, Specimen 201, that is, a multi-layered color photosensitive material comprising each of the layers of the composition shown below was prepared. (Composition of the photosensitive layer)

The coating amount was shown, for the silver-halide and colloidal silver, by the amount of silver represented by g/m^2 unit, for the coupler, additive and gelatin by the amount represented by g/m^2 unit and, for the sensitizing dye, by the mol number per one mol of silver halide in one identical layer.

First Layer (Anti-halation layer)

Black colloidal silver	0.2
Gelatin	1.3
ExM-9	0.06
UV-1	0.03
UV-2	0.06
UV-3	0.06
Solv-1	0.15
Solv-2	0.15
Solv-3	0.05

Second Layer (Intermediate layer)

Gelatin	1.0
UV-1	0.03
ExC-4	0.02
ExF-1	0.004
Solv-1	0.1
Solv-2	0.1

Third Layer (Low-sensitive red-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 4 mol%, uniform AgI type, diameter as sphere 0.5 μ, variation coefficient for the spherical diameter 20%, tabular grain, diameter/thickness ratio 3.0)	1.2 amount of silver coating
Silver iodobromide emulsion (AgI 3 mol%, uniform AgI type, diameter as sphere 0.3 μ, variation coefficient for the spherical diameter 15%, spherical grain, diameter/thickness ratio 1.0)	0.6 amount of silver coating
Gelatin	1.0
ExS-1	4.0×10^{-4}
ExS-2	5.0×10^{-4}
ExC-1	0.05
ExC-2	0.50

ExC-3	0.03
ExC-4	0.12
ExC-5	0.01

Fourth Layer (High-sensitive red-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 6 mol%, internal high AgI type, with core/shell ratio 1:1, diameter as sphere 0.7 µ, variation coefficient for the spherical diameter 15%, tabular grain, diameter/thickness ratio 4) 0.7 amount of silver coating

Gelatin	1.0
ExS-1	3.0×10^{-4}
ExS-2	2.3ÿÏ10^{-5}
ExC-6	0.11
ExC-7	0.05
ExC-4	0.05
Solv-1	0.05
Solv-2	0.05

Fifth Layer (Intermediate layer)

Gelatin	0.5
Cpd-1	0.1
Solv-1	0.05

Sixth Layer (Low-sensitive green-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 4 mol%, surface high AgI type with core/shell ratio 1:1, diameter as sphere 0.5 µ, variation coefficient for the spherical diameter 15%, tabular grains, diameter/thickness ratio 4.0) 0.35 amount of silver coating

Silver iodobromide emulsion (AgI 3 mol%, uniform AgI type, diameter as sphere 0.3 µ, variation coefficient for the spherical diameter 25%, spherical grain, diameter/thickness ratio 1.0) 0.20 amount of silver coating

Gelatin	1.0
ExS-3	5×10^{-4}
ExS-4	3×10^{-4}
ExS-5	1×10^{-4}
ExM-8	0.52
ExM-9	0.07
ExM-10	0.02
ExY-11	0.03
Solv-1	0.3
Solv-4	0.05

Seventh Layer (High-sensitive green-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 4 mol%, internal high AgI type with core/shell ratio 1:3, diameter as sphere 0.7 μ, variation coefficient for the spherical diameter 20%, tabular grains, diameter/thickness ratio 5.0)	0.8 amount of silver coating
Gelatin	0.5
ExS-3	5.0×10^{-4}
ExS-4	3.0×10^{-4}
ExS-5	1.0×10^{-4}
ExM-8	0.16
ExM-9	0.02
ExY-11	0.03
ExC-2	0.03
ExM-14	0.01
Solv-1	0.2
Solv-4	0.01

Eighth Layer (Intermediate layer)

Gelatin	0.5
Cpd-1	0.05
Solv-1	0.02

Ninth Layer (Donor layer having interlayer effect to red sensitive layer)

Silver iodobromide emulsion (AgI 2 mol%, internal high AgI type; with core/shell ratio 2:1, diameter as sphere 1.0 μ, variation coefficient for the spherical diameter 15%, tabular grain, diameter/thickness ratio 6.0)	0.35 amount of silver coating
Silver iodobromide emulsion (AgI 2 mol%, internal high AgI type of core/shell ratio 1:1, diameter as sphere 0.4 μ, variation coefficient for the spherical diameter 20%, tabular grain, diameter/thickness ratio 6.0)	0.20 amount of silver coating
Gelatin	0.5
ExS-3	8×10^{-4}
ExY-13	0.11
ExM-12	0.03
ExM-14	0.10
Solv-1	0.20

Tenth Layer (Yellow filter layer)

Yellow colloidal silver	0.05
Gelatin	0.5
Cpd-2	0.13
Solv-1	0.13
Cpd-1	0.10

Eleventh Layer (Low-sensitive blue-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 4.5 mol%, uniform AgI type, diameter as sphere 0.7 μ, variation coefficient for the spherical diameter 15%, tabular grains, diameter/thickness ratio 7.0)	0.3 amount of silver coating
Silver iodobromide emulsion (AgI 3 mol%, uniform AgI type, diameter as sphere 0.3 μ, variation coefficent for the spherical diameter 25%, tabular grains, diameter/thickness ratio 7.0)	0.15 amount of silver coating
Gelatin	1.6
ExS-6	2×10^{-4}
ExC-16	0.05
ExC-2	0.10
ExC-3	0.02
ExY-13	0.07
ExY-15	1.0
Solv-1	0.20

Twelfth Layer (High-sensitive blue-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 10 mol%, internal high AgI type, diameter as sphere 1.0 μ, variation coefficient for the spherical diameter 25%, multiple twine tabular grains, diameter/thickness ratio 2.0)	0.5 amount of silver coating
Gelatin	0.5
ExS-6	1×10^{-4}
ExY-15	0.20
ExY-13	0.01
Solv-1	0.10

Thirteenth Layer (First protective layer)

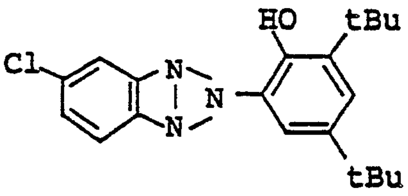
Gelatin	0.8
UV-4	0.1
UV-5	0.15
Solv-1	0.01
Solv-2	0.01

Fourteenth Layer (Second protective layer)

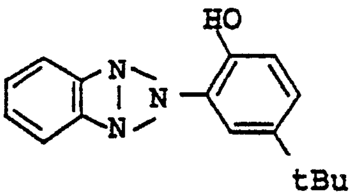
Fine grain of silver bromide emulsion (AgI 2 mol%, uniform AgI type, diameter as spheres 0.07 μ)	0.5
Gelatin	0.45
Polymethylmethacrylate (diameter 1.5 μ)	0.2
H-1	0.4
Cpd-3	0.5
Cpd-4	0.5

In addition to the ingredients described above, stabilizer Cpd-3 for the emulsion (0.04 g/m^2) and surface active agent Cpd-4 (0.01 g/m^2) were added as the coating aid to each of the layers.

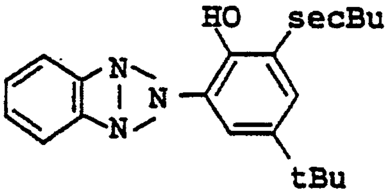
UV-1



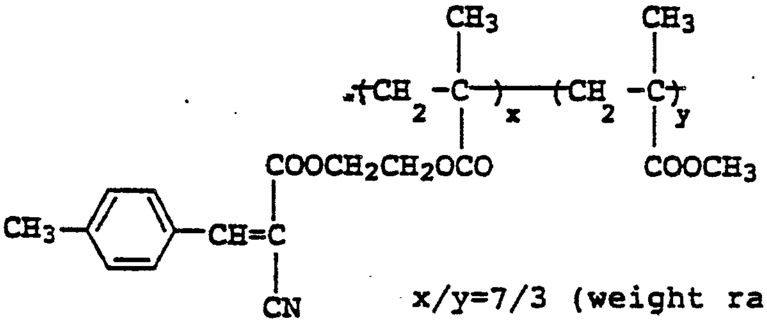
UV-2



UV-3

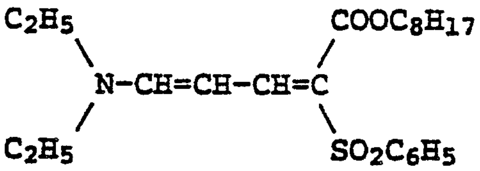


UV-4



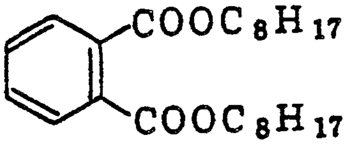
x/y=7/3 (weight ratio)

UV-5

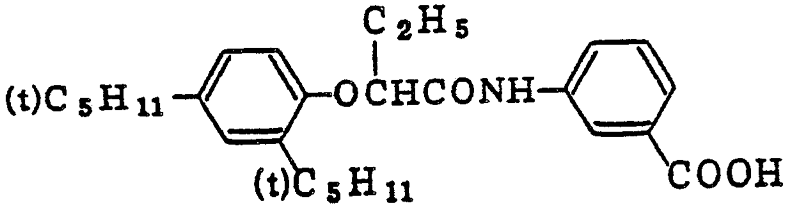


Solv-1 tricresyl phosphate
Solv-2 dibutyl phthalate

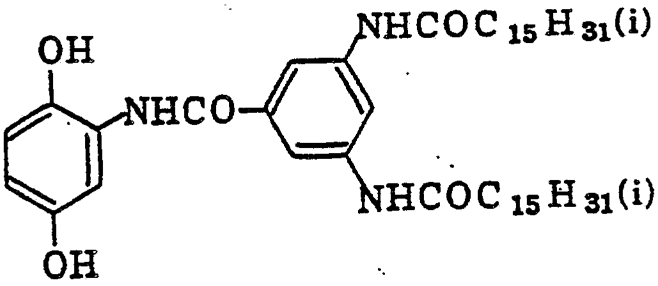
Solv-3



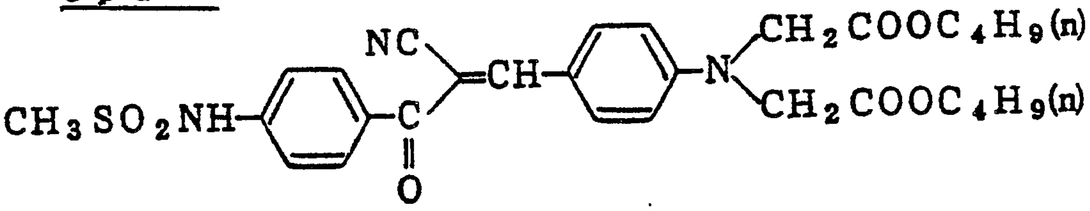
Solv-4



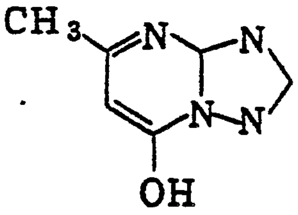
Cpd-1



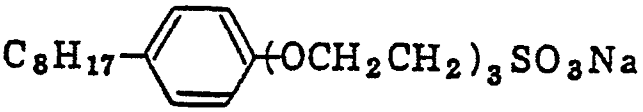
Cpd-2



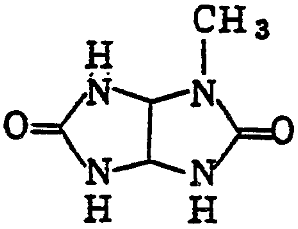
Cpd-3



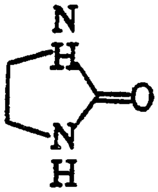
Cpd-4



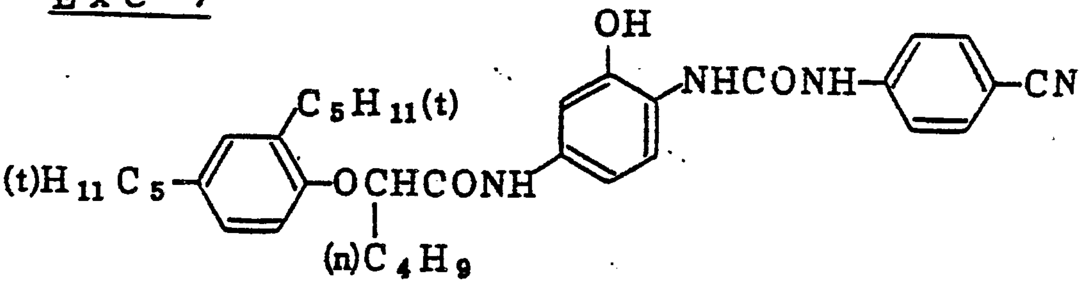
Cpd-5



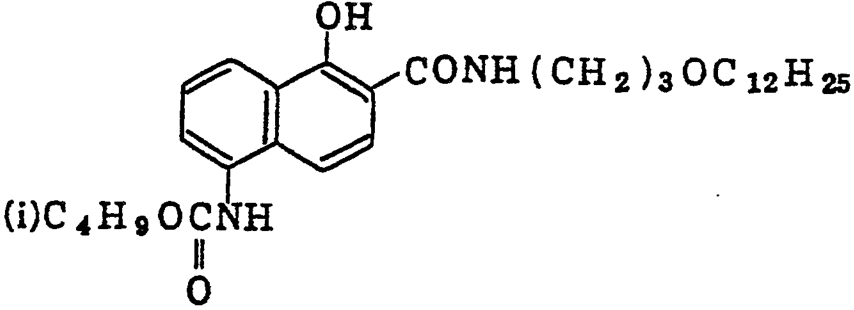
Cpd-6



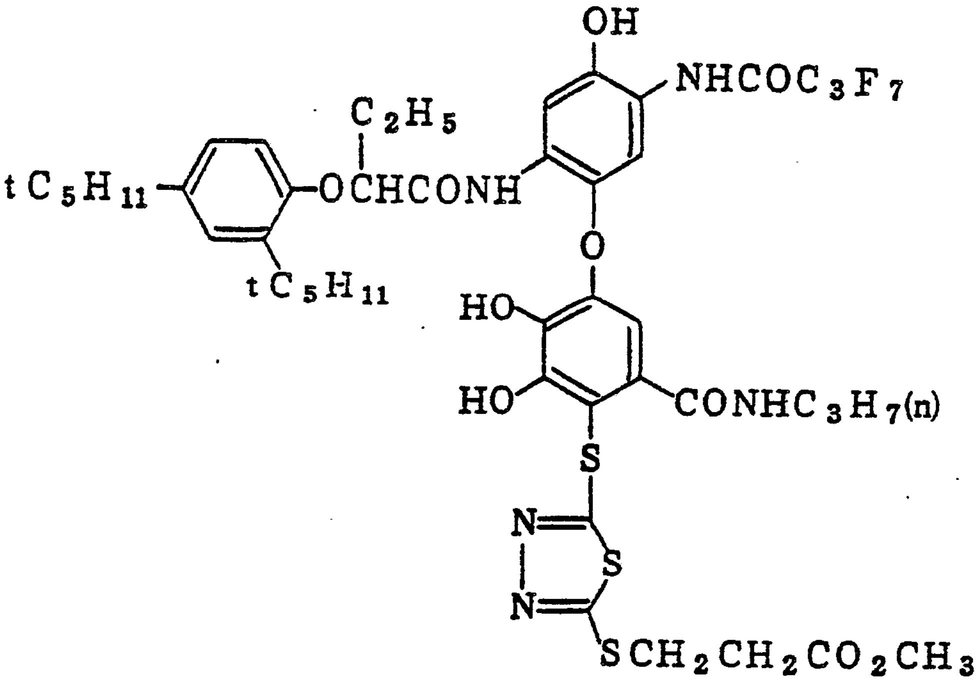
ExC-1



ExC-2



ExC-3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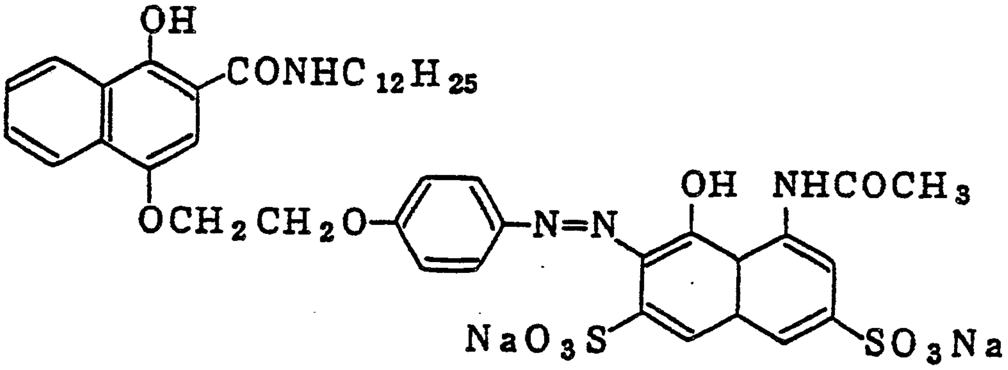
NHCOC$_3$F$_7$
C$_2$H$_5$
tC$_5$H$_{11}$
OCHCONH
tC$_5$H$_{11}$
O
HO
HO
CONHC$_3$H$_7$(n)
S
N
S
N
SCH$_2$CH$_2$CO$_2$CH$_3$

ExC-4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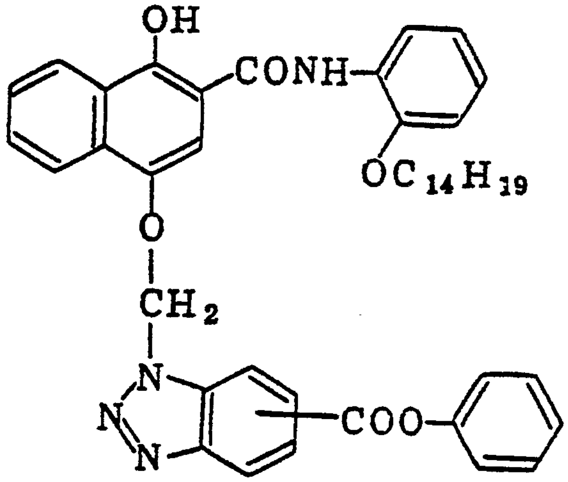
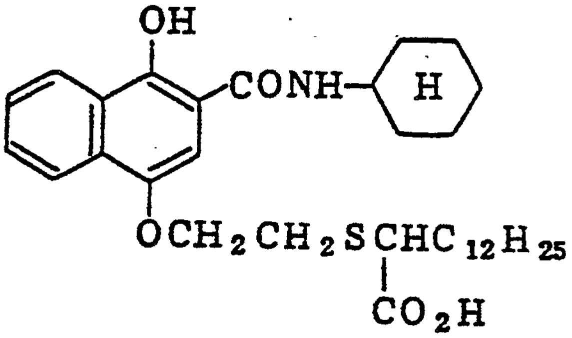
OCH$_2$CH$_2$O
N=N
OH
NHCOCH$_3$
NaO$_3$S
SO$_3$Na

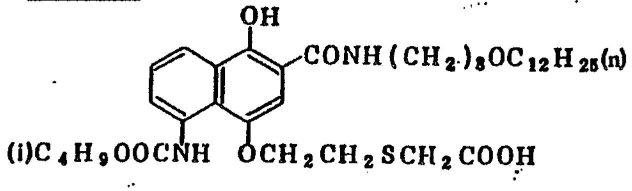
ExC-5


OH
CONH
OC14H19
O
CH2
N
N
N
COO

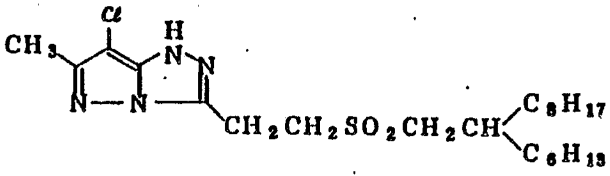
ExC-6


OH
CONH
H
OCH2CH2SCHC12H25
CO2H

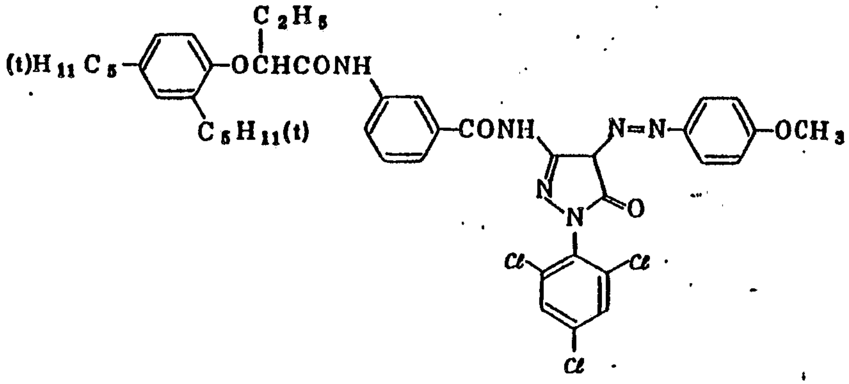
ExC−7



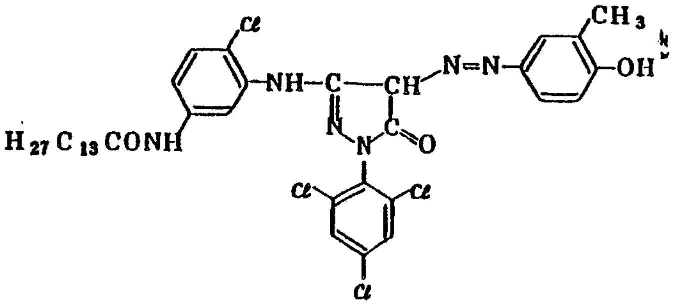
ExM−8



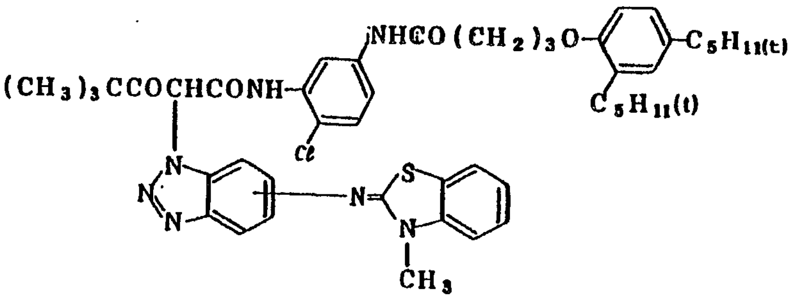
ExM−9



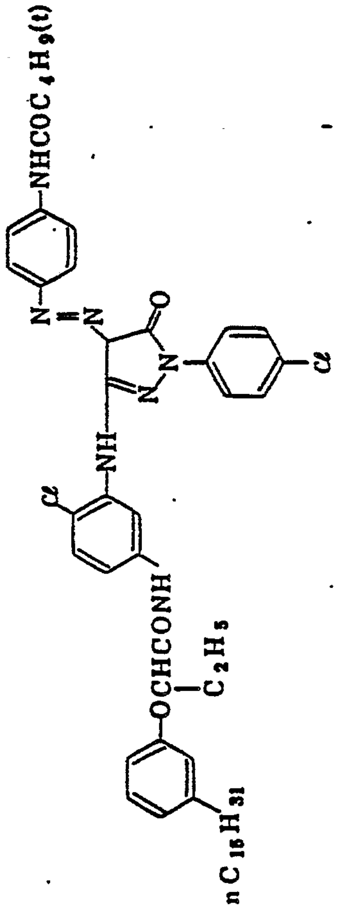
ExM−10



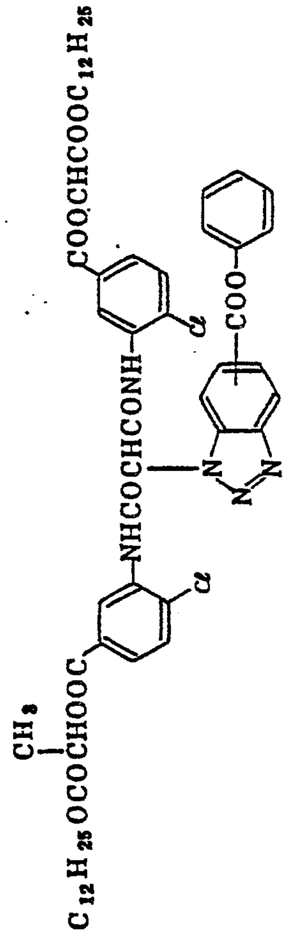
ExY−11



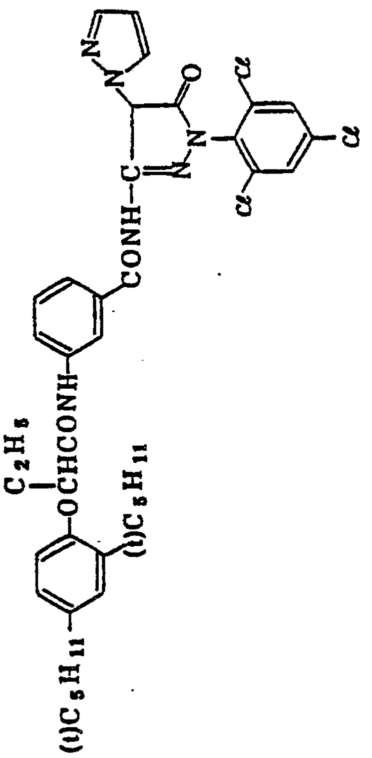
ExM−12



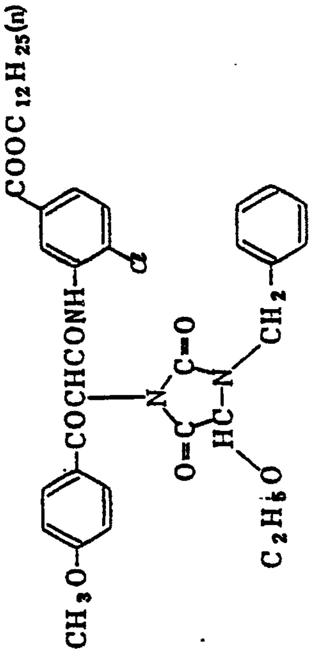
ExY−13



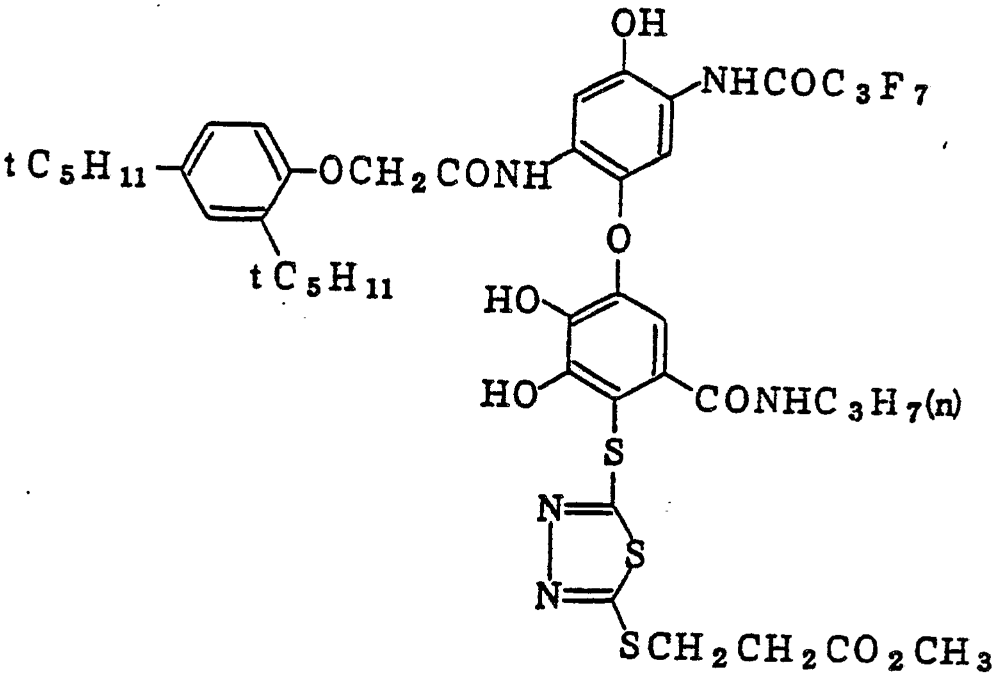
ExM−14



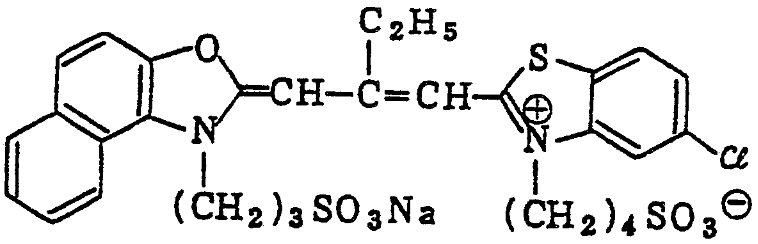
ExY−15



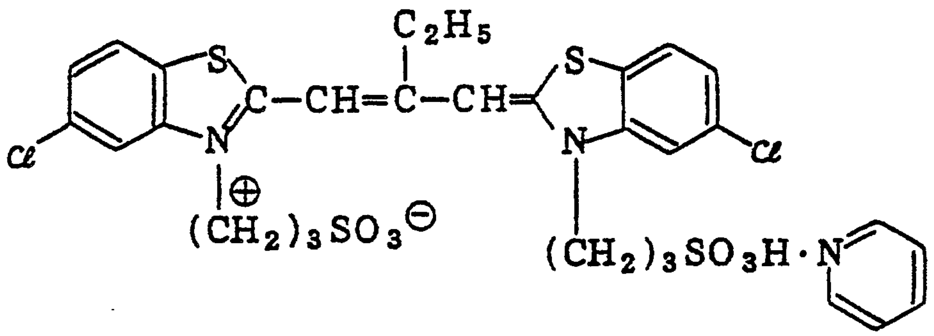
ExC－16


OH
NHCOC3F7
tC5H11
OCH2CONH
tC5H11
O
HO
HO
CONHC3H7(n)
S
N
S
N
SCH2CH2CO2CH3

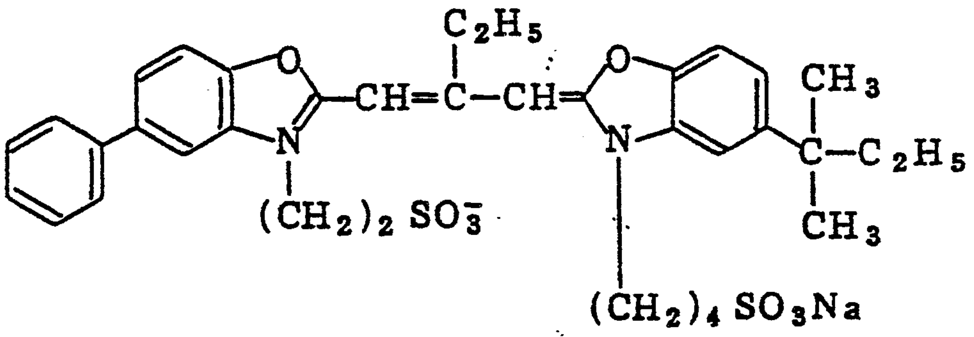
ExS－1


C2H5
O
CH－C＝CH
S
N
N
(CH2)3SO3Na
(CH2)4SO3
Cl

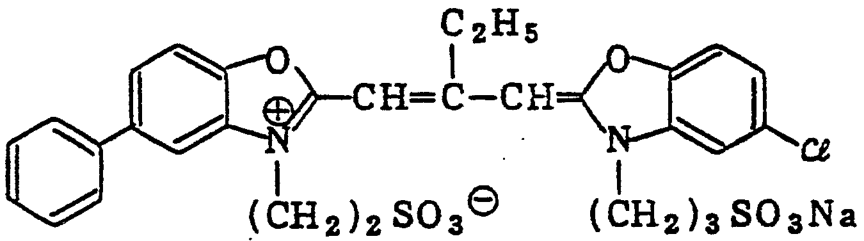
ExS−2



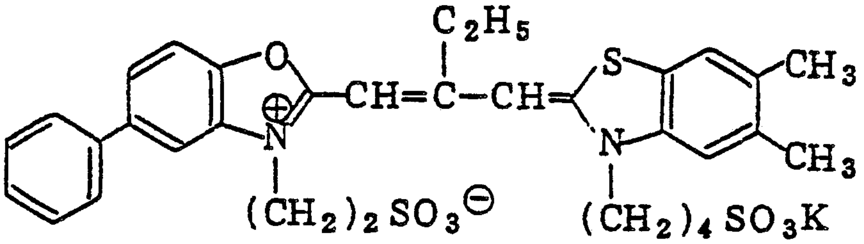
ExS−3



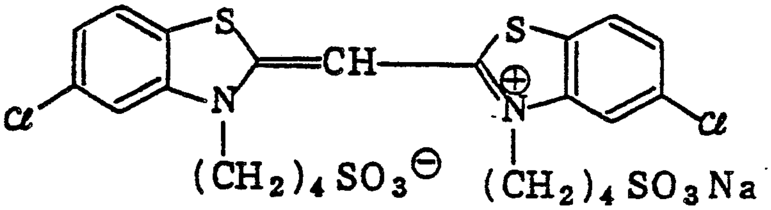
ExS−4



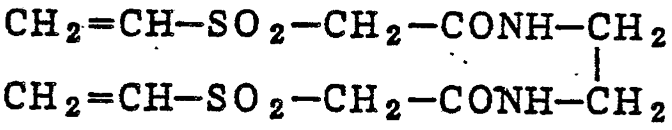
ExS-5



ExS-6

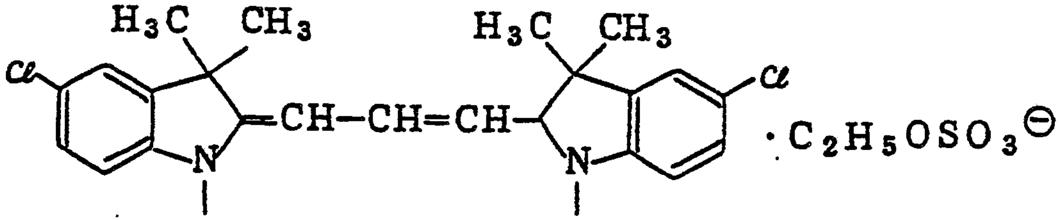


H-1



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

ExF-1



Specimens 202 to 210

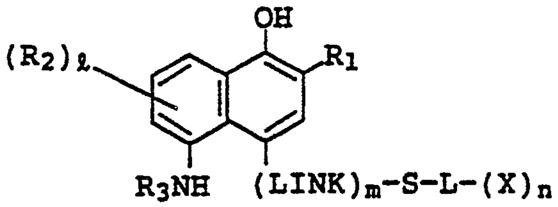
Specimens 202 to 210 were prepared by replacing the coupler EXC-6 added to the fourth layer in Specimen 201 with the comparative coupler and the coupler of the present invention used in Example 1.

When the same test as that in Example 2 was applied to the obtained Specimens 201 to 210, substantially the same effects could be obtained.

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

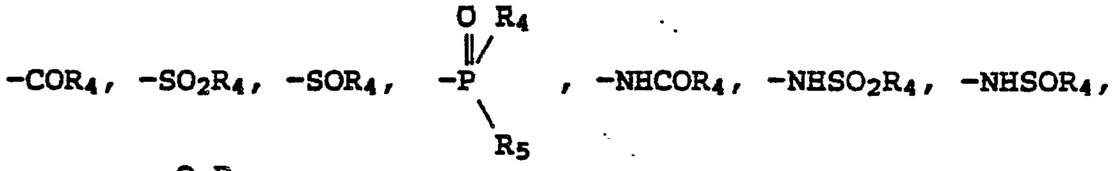
Claims

1. A silver halide color photosensitive material comprising at least one silver halide emulsion layer on a support, which contains at least one bleaching accelerator releasing type coupler represented by the following Formula (I):

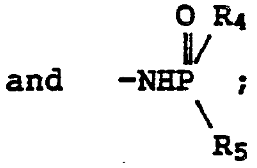


(I)

wherein R_1 is selected from the group consisting of a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an amidino group, a guanidino group,

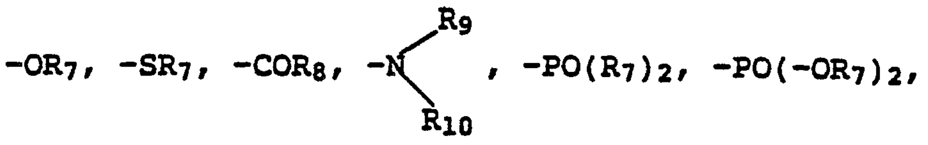


$$-COR_4,\ -SO_2R_4,\ -SOR_4,\ -\overset{O}{\overset{\|}{P}}(R_4)R_5,\ -NHCOR_4,\ -NHSO_2R_4,\ -NHSOR_4,$$

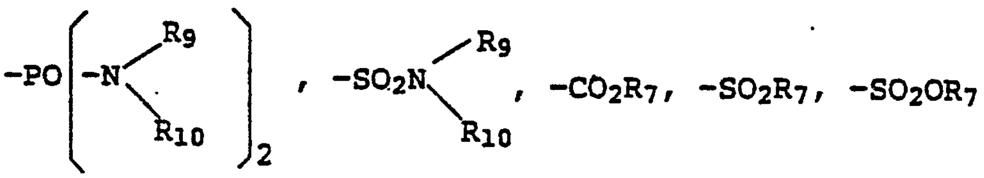


$$\text{and}\quad -NH\overset{O}{\overset{\|}{P}}(R_4)R_5\ ;$$

R_2 is selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a sulfo group, an amino group, a cyano group, a nitro group, an aliphatic group, an aromatic group, a carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a ureido group, an acyl group, an acyloxy group, an aliphatic oxy group, an aromatic oxy group, an aliphatic thio group, an aromatic thio group, an aliphatic sulfonyl group, an aromatic sulfonyl group, an aliphatic sulfinyl, an aromatic sulfinyl group, an aliphatic oxy carbonyl group, an aromatic oxy carbonyl group, an aliphatic oxy carbonylamino group, an aromatic oxy carbonylamino group, a sulfamoyl amino group, a heterocyclic group and an imido group; ℓ represents an integer of 0 to 3; R_3 is selected from the group consisting of a hydrogen atom and R_6Y; LINK represents a functional linkage group connecting by way of a hetero atom to the 4-position of a naphthol ring; m represents 0 or 1; L is selected from the group consisting of a (n+1) valent group, that is, an alkyl group with 1 to 8 carbon atoms, an aromatic group with 6 to 10 carbon atoms, and a heterocyclic group with 1 to 10 carbon atoms each removed with hydrogen atoms by the number of n; X represents a water soluble substituent; n represents an integer 1 to 3, provided that:
R_4 and R_5 are both selected independently from the group consisting of an aliphatic group, an aromatic group, a heterocyclic group, an amino group, an aliphaticoxy group or an aromaticoxy group, R_6 is selected from the group consisting of a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group,



$$-OR_7,\ -SR_7,\ -COR_8,\ -N\begin{matrix}R_9\\R_{10}\end{matrix},\ -PO(R_7)_2,\ -PO(-OR_7)_2,$$



$$-PO\left(-N\begin{matrix}R_9\\R_{10}\end{matrix}\right)_2,\ -SO_2N\begin{matrix}R_9\\R_{10}\end{matrix},\ -CO_2R_7,\ -SO_2R_7,\ -SO_2OR_7$$

and $-CO_2R_7$, $-SO_2R_7$, $-SO_2OR_7$ and an imido group; Y is selected from the group consisting of $>N-R_9$, -CO-, $-SO_2-$, -SO- and a single bond; R_7 is selected from the group consisting of an aliphatic group, an aromatic group and a heterocyclic group; R_8 is selected from the group consisting of a hydrogen atom, an aliphatic group, an aromatic group and a heterocyclic group; R_9 and R_{10} are both selected independently from the group consisting of a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an aliphatic sulfonyl group and an aromatic sulfonyl group; and provided that:

in a case where ℓ is 2 more, each R_2 may be identical to or different from the other, or any R_2 may join with another R_2 to form a ring, and an R_2 may form a dimer or higher polymeric form which is obtained by way of a divalent or higher valent group in any of R_1, R_2, or R_3.

2. The material of Claim 1, wherein R_1 represents a halogen atom, $-COR_4$ or $-SO_2R_4$.

3. The material of Claim 2, wherein R_4 represents an amino group.

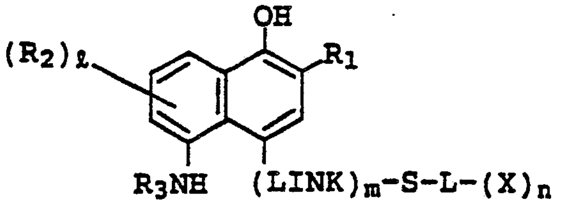
4. The material of Claim 1, wherein ℓ represents 0.

5. The material of Claim 1, wherein R_6 represents an aliphatic group, an aromatic group, $-OR_7$, or SR_7 and Y represents -CO- or $-SO_2-$.

6. The material of Claim 1, whrerein X is a substituent in which π-substituent constant is 0.5 or less.

7. The material of Claim 1, wherein n represents 1.

8. A method of processing a silver halide color photosensitive material wherein a sivler halide color photosensitive material comprising at least one silver halide emulsion layer on a support and containing at least one bleach accelerator releasing type coupler represented by Formula (1):



(I)

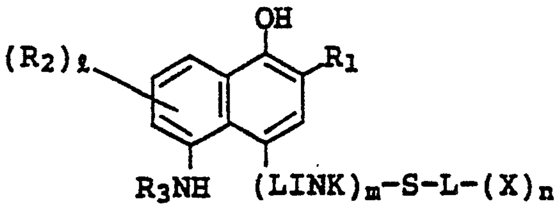
is processed in a bleach-fix bath without water washing after color development.

9. The method of Claim 8, wherein the pH value of the bleach-fix bath is 5.7 or less.

10. The method of Clam 8, wherein the bleaching agent used in said bleach-fix bath is selected from the group consisting of:

(1) Diethylenetriamine pentaacetic acid
(2) Pentasodium salt of diethylenetriamine pentaacetic acid
(3) Ethylenediamine-N-(β-oxyethyl)-N,N′,N′-triacetic acid
(4) Trisodium ethylenediamine-N-(β-oxyethyl)-N,N′,N′-triacetate
(5) Triammonium ethylenediamine-N-(β-oxyethyl)-N,N′,N′-triacetate
(6) 1,2-diaminopropane tetraacetic acid
(7) Disodium 1,2-diaminopropane tetraacetate
(8) Nitrilotriacetic acid
(9) Sodium nitrilotriacetic acid salt
(10) Cyclohexanediamine tetraacetate
(11) Cyclohexanediamine tetraacetic acid disodium salt
(12) N-methyliminodiacetic acid
(13) Iminodiacetic acid
(14) Dihydroxyethyl glycine
(15) Ethylether diamine tetraacetic acid
(16) Glycol ether diamine tetraacetic acid
(17) Ethylenediamine tetrapropionic acid
(18) 1,3-diaminopropane tetraacetic acid and
(19) Ethylenediamine tetra-acetic acid.

11. A method of processing a silver halide color photosensitive material, wherein the method comprises a step of applying water washing or stabilization directly after the fixing or bleach-fix processing to the silver halide color photosensitive material, which material has at least one silver halide emulsion layer on a support and contains at least one bleaching accelerator releasing type coupler represented by Formula (I):



(I)

the water washing or the stabilization step includes a plurality of vessels and, upon replenishing a processing solution in a multi-stage counter current system, the replenishing amount is from 0.1 to 50 times of the amount of the processing solution carried from the preceeding bath per unit area of the silver halide color photosensitive material to be processed.