(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 341 034 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
03.09.2003 Bulletin 2003/36

(51) Int Cl.7: **G03C 7/30**

(21) Application number: **03004333.5**

(22) Date of filing: **28.02.2003**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PT SE SI SK TR
Designated Extension States:
AL LT LV MK RO

(30) Priority: **01.03.2002 JP 2002056655**
28.03.2002 JP 2002092955

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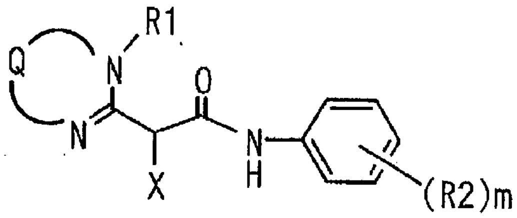
(54) Silver halide color photographic light-sensitive material

(57) A silver halide color photographic light-sensitive material comprising a yellow dye-forming coupler represented by the following formula (I), in combination with at least one specific additive, in at least one layer provided on a support:

formula (I)



wherein, in formula (I), Q represents a group of non-metal atoms that form a 5- to 7-membered ring in combination with the -N=C-N(R1)-; R1 and R2 represent a substituent; m represents an integer of 0 to 5; and X represents a hydrogen atom, or a group capable of being split-off upon a coupling reaction with an oxidized product of a developing agent.

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a silver halide photographic light-sensitive material. Particularly, the present invention relates to a silver halide color photographic light-sensitive material that is excellent in color reproduction and image storability (preservability).

BACKGROUND OF THE INVENTION

[0002] In a silver halide photographic light-sensitive material (hereinafter, also referred to simply as "a light-sensitive material") for subtractive color photography, a color image is formed by dyes of three primary colors of yellow, magenta, and cyan. In the color photography that uses current p-phenylenediamine-series color-developing agents, acylacetoanilide-series compounds are used as a yellow coupler. However, the hue of the yellow dyes obtained from these yellow couplers becomes reddish, due to an inferior sharpness of a peak of the absorption curve at the longer wavelength side (that is, on the absorption curve, the peak in interest has subsidiary absorption at its foot portion at the longer wavelength side), which renders it difficult to obtain a yellow hue with high purity. Further, because the molecular extinction coefficient of the yellow dyes is low, it is necessary, to attain a desired color density, to use larger amounts of both the coupler and the silver halide. The use of such larger amounts of these components raises the problem that the resulting increase in thickness of a light-sensitive material sometimes lowers the sharpness of the obtained color image. Further, the above-mentioned dyes are sometimes easily decomposed under conditions of high temperature and high humidity, or under long-time light irradiation, and thus they have insufficient image storability after development processing. Therefore, it has been desired to improve on these problems.

[0003] In order to solve these problems, improvement of acyl groups and anilido groups were proposed on the couplers. Recently, as improved couplers of the conventional acylacetoanilide-series couplers, there were proposed, for example, 1-alkylcyclopropanecarbonyl acetoanilide-series compounds, described in JP-A-4-218042 ("JP-A" means unexamined published Japanese patent application); cyclomalonic acid diamide-type couplers, described in JP-A-5-11416; pyrrole-2- or 3-yl- or indole-2- or 3-yl- carbonylacetoanilide-series couplers, described in, for example, European Patent Publication Nos. 953870A1, 953871A1, 953872A1, 953873A1, 953874A1 and 953875A1. The dyes formed from these couplers were improved in terms of both hue and molecular extinction coefficient of dyes formed, compared with the conventional ones. However, they are not satisfactory in image storability still. Further, owing to their complicated chemical structure, the synthesis route became longer, and consequently cost of the couplers became higher, causing a practical problem. In addition, U.S. Patent No. 3,841,880, JP-A-52-82423 and JP-A-2-28645 propose acetate ester-series and acetoanilide-series couplers to which 1,2,4-benzothiadiazine-1,1-dioxide is bonded. However, these couplers are low in color-forming property, they are inferior in sharpness of a peak of the absorption curve owing to the foot portion on the longer wavelength side, and they are low in image fastness. Therefore, improvement of these properties has been desired.

SUMMARY OF THE INVENTION

[0004] An object of the present invention is to provide a silver halide photographic light-sensitive material that overcomes the above-mentioned problems. Another object of the present invention is to provide a silver halide photographic light-sensitive material that has excellent color-forming property and gives dyes of excellent hue and high-grade storability, whereby neither a white background portion nor a dye image portion become discolored or fade for a long time. Still another object of the present invention is to provide a silver halide photographic light-sensitive material that provides not only excellent color-forming property and hue of dye but also little fog and color mixing, a dye image that will not change for a long time, and little fluctuation of color-forming property even after long-term storage after coating (good virgin stock storability). Further another object of the present invention is to provide a silver halide color photographic light-sensitive material that provides not only excellent color-forming property and hue of dye but also excellent in development processing stability, and dye image formed will not discolor for a long time.

[0005] Other and further objects, features and advantages of the invention will appear more fully from the following description.

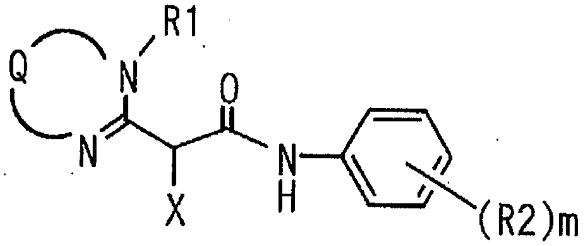
DETAILED DESCRIPTION OF THE INVENTION

[0006] As a result of intensive studies, the present inventors have found that the above-mentioned problems can be solved by employing, in at least one layer provided on a support, at least one yellow dye-forming coupler represented by formula (I) described below, in combination with at least one compound selected from the group consisting of metal complexes and compounds represented by any one of the following formulae (TS-I), (TS-II), (TS-III), (TS-IV), (TS-V), and (TS-VI) shown below. The present invention is made on the basis of this finding.

[0007] According to the present invention, there are provided:

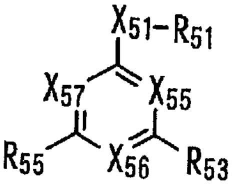
(1) A silver halide color photographic light-sensitive material comprising at least one yellow dye-forming coupler represented by formula (I) shown below, and at least one compound selected from the group consisting of a metal complex and a compound represented by any one of the formulae (TS-I), (TS-II), (TS-III), (TS-IV), (TS-V), and (TS-VI) shown below, in at least one layer provided on a support:

formula (I)

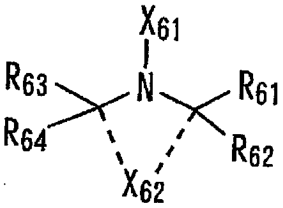


wherein, in formula (I), Q represents a group of non-metal atoms that form a 5- to 7-membered ring in combination with the -N=C-N(R1)-; R1 represents a substituent; R2 represents a substituent; m represents an integer of 0 to 5; when m is 2 or more, the multiple R2s may be the same or different, and the R2s may bond each other to form a ring; and X represents a hydrogen atom, or a group capable of being split-off upon a coupling reaction with an oxidized product of a developing agent;

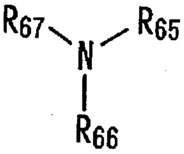
formula (TS-I)



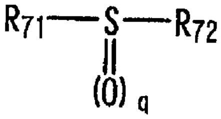
formula (TS-II)



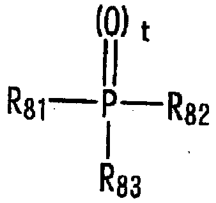
formula (TS-III)



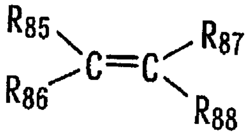
formula (TS-IV)



formula (TS-V)



formula (TS-VI)



wherein, in formula (TS-I), R_{51} represents a hydrogen atom, an aliphatic group, an aryl group, a heterocyclic group, an acyl group, an aliphatic oxycarbonyl group, an aryl oxycarbonyl group, an aliphatic sulfonyl group, an aryl sulfonyl group, a phosphoryl group, or -Si(R_{58})(R_{59})(R_{60}), in which R_{58}, R_{59}, and R_{60} each independently represent an aliphatic group, an aryl group, an aliphatic oxy group, or an aryloxy group; X_{51} represents -O-, or -N(R_{57})-, in which R_{57} has the same meaning as R_{51}; X_{55} represents -N=, or -C(R_{52})=; X_{56} represents -N=, or -C(R_{54})=; X_{57} represents -N=, or -C(R_{56})=; R_{52}, R_{53}, R_{54}, R_{55}, and R_{56} each independently represent a hydrogen atom, or a substituent; each combination of R_{51} and R_{52}, R_{57} and R_{56}, and R_{51} and R_{57} may combine together to form a 5- to 7-membered ring; each combination of R_{52} and R_{53}, and R_{53} and R_{54} may combine together to form a 5- to 7-membered ring, or a spiro ring, or a bicyclo ring; wherein the total number of carbon atoms of the compound represented by formula (TS-I) is 10 or more; and when, in formula (I), a 4-pyrimidone ring is formed by Q, and R1 is an alkyl group having 1 to 6 carbon atoms, any one of X_{55}, X_{56} and X_{57} is -N=; with the proviso that all of R_{51} to R_{57} simultaneously do not represent a hydrogen atom;

wherein, in formula (TS-II), R_{61}, R_{62}, R_{63}, and R_{64} each independently represent a hydrogen atom, or an aliphatic group; each combination of R_{61} and R_{62}, and R_{63} and R_{64} may combine together to form a 5- to 7-membered ring; X_{61} represents a hydrogen atom, an aliphatic group, an aliphatic oxy group, an aliphatic oxycarbonyl group, an aryl oxycarbonyl group, an acyl group, an acyloxy group, an aliphatic oxycarbonyloxy group, an aryl oxycarbonyloxy group, an aliphatic sulfonyl group, an aryl sulfonyl group, an aliphatic sulfinyl group, an aryl sulfinyl group, a sulfamoyl group, a carbamoly group, a hydroxy group, or an oxy radical group; X_{62} represents a group of non-metal atoms necessary to form a 5- to 7-membered ring; and when, in formula (I), Q forms a 4-pyrimidone ring and R1 is an alkyl group having 1 to 6 carbon atoms, X_{61} represents a hydrogen atom, an aliphatic group, an aliphatic oxy group, an aliphatic oxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, an aliphatic oxycarbonyloxy group, an aryl oxycarbonyloxy group, an aliphatic sulfonyl group, an aryl sulfonyl group, an aliphatic sulfinyl group, an aryl sulfinyl group, a sulfamoyl group, a carbamoly group, a hydroxyl group, or an oxy radical group;

wherein, in formula (TS-III), R_{65} and R_{66} each independently represent a hydrogen atom, an aliphatic group, an aryl group, an acyl group, an aliphatic oxycarbonyl group, an aryl oxycarbonyl group, a carbamoly group, an aliphatic sulfonyl group, or an aryl sulfonyl group; R_{67} represents a hydrogen atom, an aliphatic group, an aliphatic oxy group, an aryloxy group, an aliphatic thio group, an arylthio group, an acyloxy group, an aliphatic oxycarbonyloxy group, an aryl oxycarbonyloxy group, a substituted amino group, a heterocyclic group, or a hydroxyl group; each combination of R_{65} and R_{66}, and R_{66} and R_{67}, and R_{65} and R_{67} may combine together to form a 5-to 7-membered ring except 2,2,6,6-tetraalkylpyridine skeleton; and the total number of carbon atoms of R_{65} and R_{66} is 7 or more; with the proviso that all of R_{65} and R_{66} simultaneously do not represent a hydrogen atom;

wherein, in formula (TS-IV), R_{71} represents a hydrogen atom, an aliphatic group, an aryl group, a heterocyclic group, Li, Na, or K; R_{72} represents an aliphatic group, an aryl group, or a heterocyclic group; R_{71} and R_{72} may combine together to form a 5- to 7-membered ring; q represents 0, 1 or 2; wherein the total number of carbon atoms of R_{71} and R_{72} is 10 or more;

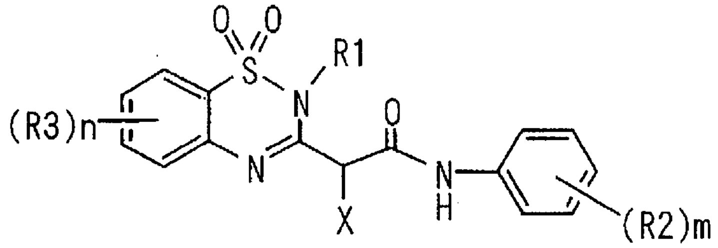
wherein, in formula (TS-V), R_{81}, R_{82}, and R_{83} each independently represent an aliphatic group, an aryl group, an aliphatic oxy group, an aryloxy group, an aliphatic amino group, or an aryl amino group; t represents 0 or 1; each combination of R_{81} and R_{82}, and R_{81} and R_{83} may combine together to form a 5- to 8-membered ring; wherein the total number of carbon atoms of R_{81}, R_{82}, and R_{83} is 10 or more; and

wherein, in formula (TS-VI), R_{85}, R_{86}, R_{87}, and R_{88} each independently represent a hydrogen atom, or a substituent, and any two of R_{85}, R_{86}, R_{87} and R_{88} may combine together to form a 5- to 7-membered ring except an aromatic ring only consisting of carbon atoms as a skeleton atom; and the total number of carbon atoms of the compound represented by formula (TS-VI) is 10 or more; with the proviso that all of R_{85}, R_{86}, R_{87}, and R_{88} simultaneously do not represent a hydrogen atom.

(2) The silver halide color photographic light-sensitive material according to the above item (1), wherein Q in the above-mentioned formula (I) is a group represented by -C(-R11)=C(-R12)-SO_2- or -C(-R11)=C(-R12)-CO-, in which R11 and R12 are groups that bond with each other to form a 5- to 7-membered ring together with -C=C-, or they each independently represent a hydrogen atom or a substituent.

(3) The silver halide color photographic light-sensitive material according to the above item (1) or (2), wherein the yellow dye-forming coupler represented by formula (I) is a yellow dye-forming coupler represented by formula (II):

formula (II)



wherein, in formula (II), R1 represents a substituent; R2 represents a substituent; m represents an integer of 0 to 5; when m is 2 or more, the multiple R2s may be the same or different, and the R2s may bond each other to form a ring; R3 represents a substituent; n represents an integer of 0 to 4; when n is 2 or more, the multiple R3s may be the same or different, and the R3s may bond each other to form a ring; and X represents a hydrogen atom, or a group capable of being split-off upon a coupling reaction with an oxidized product of a developing agent.

(4) The silver halide color photographic light-sensitive material according to the above item (3),

wherein, in the dye-forming coupler represented by the above-mentioned formula (II), R1 is a substituted or unsubstituted alkyl group.

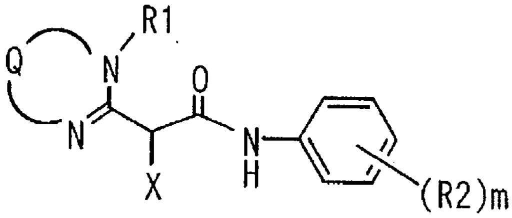
[0008] The present invention is explained below in detail.

[0009] The term "aliphatic group" used in the present specification means such groups, in which the aliphatic portion may be a saturated or unsaturated, straight chain, branched chain, or a cycle, and the aliphatic portion embraces, for example, an alkyl group, an alkenyl group, a cycloalkyl group, and a cycloalkenyl group; and these can be unsubstituted or substituted. Further, the term "aryl group" used herein means a substituted or unsubstituted, monocyclic or condensed ring. The term "heterocyclic group" used herein means such groups, in which the heterocycle portion contains a hetero atom(s) (such as nitrogen, sulfur and oxygen atoms) in the ring skeleton, and the heterocycle embraces a substituted or unsubstituted, saturated or unsaturated, and monocyclic or condensed ring.

[0010] The term "substituent" used in the present specification means any groups or atoms that are able to substitute for other groups or atoms; and embraces, for example, an aliphatic group, an aryl group, a heterocyclic group, an acyl group, an acyloxy group, an acylamino group, an aliphatic oxy group, an aryloxy group, a heterocyclic oxy group, an aliphatic oxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, a carbamoyl group, an aliphatic sulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an aliphatic sulfonyloxy group, an arylsulfonyloxy group, a heterocyclic sulfonyloxy group, a sulfamoyl group, an aliphatic sulfonamido group, an aryl sulfonamido group, a heterocyclic sulfonamido group, an amino group, an aliphatic amino group, an arylamino group, a heterocyclic amino group, an aliphatic oxycarbonylamino group, an aryloxycarbonylamino group, a heterocyclic oxycarbonylamino group, an aliphatic sulfinyl group, an aryl sulfinyl group, an aliphatic thio group, an arylthio group, a hydroxy group, a cyano group, a sulfo group, a carboxyl group, an aliphatic oxyamino group, an aryloxyamino group, a carbamoylamino group, a sulfamoylamino group, a halogen atom, a sulfamoylcarbamoyl group, a carbamoylsulfamoyl group, a dialiphatic oxyphosphinyl group, and a diaryloxyphosphinyl group.

[0011] First, the compound represented by formula (I) for use in the present invention is explained in detail. In the present specification, the compound is also referred to as a dye-forming coupler.

formula (I)



[0012] In formula (I), R1 represents a substituent other than a hydrogen atom. Examples of the substituent include a halogen atom, an alkyl group (including a cycloalkyl group and a bicycloalkyl group), an alkenyl group (including a cycloalkenyl group and a bicycloalkenyl group), an alkynyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, a nitro group, a carboxyl group, an alkoxy group, an aryloxy group, a silyloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group (including an alkylamino group and an anilino group), an acylamino group, an aminocarbonylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfamoylamino group, an alkyl- or aryl-sulfonylamino group, a mercapto group, an alkylthio group, an arylthio group, a heterocyclic thio group, a sulfamoyl group, a sulfo group, an alkyl- or aryl-sulfinyl group, an alkyl- or aryl-sulfonyl group, an acyl group, an aryloxycarbonyl group, an alkoxycarbonyl group, a carbamoyl group, an arylazo group, a heterocyclic azo group, an imido group, a phosphino group, a phosphinyl group, a phosphinyloxy group, a phosphinylamino group, and a silyl group.

[0013] The above-mentioned substituent may be further substituted with another substituent. Examples of this another substituent are the same to the above-mentioned examples of the substituent.

[0014] R1 is preferably a substituted or unsubstituted alkyl group. The total number of carbon atoms of R1 is preferably in the range of 1 to 60, more preferably in the range of 6 to 50, still more preferably in the range of 11 to 40, and most preferably in the range of 16 to 30. In the case that R1 is a substituted alkyl group, examples of the substituent of the alkyl group include those atoms and groups exemplified as the substituent of the above-mentioned R1.

[0015] The number of carbon atoms in the alkyl group itself according to R1 is preferably in the range of 1 to 40, more preferably in the range of 3 to 36, and furthermore preferably in the range of 8 to 30. This preferable order does not particularly depend on Q, but this order is preferably applied in the case where Q described below is a group represented by -C(-R11)=C(-R12)-CO-.

[0016] R1 is preferably an unsubstituted alkyl group having 11 or more carbon atoms, or an alkyl group substituted with an alkoxy group or aryloxy group at the 2-, 3- or 4-position, more preferably an unsubstituted alkyl group having 16 or more carbon atoms, or an alkyl group substituted with an alkoxy group or aryloxy group at the 3-position, and most preferably a $C_{16}H_{33}$ group, a $C_{18}H_{37}$ group, a 3-lauryloxypropyl group, or 3-(2,4-di-t-amylphenoxy)propyl group.

[0017] In formula (I), Q represents a group of non-metal atoms that forms a 5- to 7-membered ring in combination with the -N=C-N(R1)-. Preferably, the 5- to 7-membered ring thus formed is a substituted or unsubstituted, and monocyclic or condensed heterocycle. More preferably, the ring-forming atoms are selected from carbon, nitrogen and sulfur atoms. Still more preferably, Q represents a group represented by -C(-R11)=C(-R12)-SO_2- or -C(-R11)=C(-R12)-CO- (in the present invention, these expressions of the foregoing group do not limit the bonding orientation of the group in formula (I), to the ones shown by these expressions). R11 and R12 are groups that bond each other to form a 5- to 7-membered ring together with the -C=C-moiety, or R_{11} and R_{12} each independently represent a hydrogen atom or a substituent. The 5- to 7-membered ring thus formed may be saturated or unsaturated, and the ring may be an alicyclic, aromatic or heterocyclic ring. Examples of the ring include benzene, furan, thiophene, cyclopentene, and cyclohexane rings. Further, examples of the substituent represented by R11 or R12 are those enumerated as the substituent of the above-described R1.

[0018] In the present invention, Q is especially preferably a group represented by -C(-R11)=C(-R12)-SO_2-. (R11 and R12 have the same meanings as described in the above.)

[0019] These substituents and the rings formed through bonding of multiple substituents may be further substituted with another substituent. Examples of this another substituent are the same as described as the examples of the above-mentioned substituent of R1.

[0020] In formula (I), R2 represents a substituent other than a hydrogen atom. Examples of the substituent include those exemplified as the substituent of the above-mentioned R1. R2 is preferably a halogen atom (i.e., fluorine, chlorine, bromine), an alkyl group (e.g., methyl, isopropyl), an aryl group (e.g., phenyl, naphthyl), an alkoxy group (e.g., methoxy, isopropyloxy), an aryloxy group (e.g., phenoxy), an acyloxy group (e.g., acetyloxy), an amino group (e.g., dimethylamino, morpholino), an acylamino group (e.g., acetoamido), a sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido), an alkoxycarbonyl group (e.g., methoxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), a carbamoyl group (e.g., N-methylcarbamoyl, N,N-diethylcarbamoyl), a sulfamoyl group (e.g., N-methylsulfamoyl, N, N-diethylsulfamoyl), an alkylsulfonyl group (e.g., methane sulfonyl), an arylsulfonyl group (e.g., benzene sulfonyl), a cyano group, a carboxyl group, or a sulfo group. When R2 is at the ortho position to the -CONH- group, R2 is preferably a halogen atom, an alkoxy group, an aryloxy group, or an alkyl group.

[0021] In the present invention, it is preferable that at least one R2 is at the ortho position to the -CONH- group.

[0022] In formula (I), m represents an integer of 0 or more and 5 or less. When m is 2 or more, R2s may be the same or different, and they may combine together to form a ring.

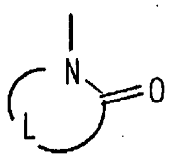
[0023] m is preferably in the range of 0 to 3, more preferably in the range of 0 to 2, further more preferably 1 or 2, and most preferably 2.

[0024] In formula (I), X represents a hydrogen atom, or a group that can be split-off upon a coupling reaction with an oxidized product of a developing agent. Examples of the group capable of being split-off upon a coupling reaction with an oxidized product of a developing agent include a group capable of being split-off with a nitrogen, oxygen, or sulfur atom (a splitting-off atom), and a halogen atom (e.g., chlorine, bromine).

[0025] Examples of the group that splits off with a nitrogen atom include a heterocyclic group (preferably 5-to 7-membered substituted or unsubstituted saturated or unsaturated aryl (herein the term "aryl" is used to embrace a substance that has (4n+2) cyclic conjugated electrons) or non-aryl, monocyclic or condensed heterocyclic groups, more preferably a 5- or 6-membered heterocyclic group, in which the ring-forming atoms are selected from carbon, nitrogen and sulfur atoms and in addition at least one of hetero atoms selected from nitrogen, oxygen and sulfur atoms is incorporated, with specific examples of the heterocyclic group including succinimide, maleinimide, phthalimide, diglycolimide, pyrrole, pyrazole, imidazole, 1,2,4-triazole, tetrazole, indole, benzopyrazole, benzimidazole, benzotriazole, imidazoline-2,4-dione, oxazolidine-2,4-dione, thiazolidine-2-one, benzimidazoline-2-one, benzoxazoline-2-one, benzothiazoline-2-one, 2-pyrroline-5-one, 2-imidazoline-5-one, indoline-2,3-dione, 2,6-dioxypurine parabanic acid, 1,2,4-triazolidine-3,5-dione, 2-pyridone, 4-pyridone, 2-pyrimidone, 6-pyridazone, 2-pyrazone, 2-amino-1,3,4-thiazolidine-4-one), a carbonamido group (e.g., acetamido, trifluoroacetamido), a sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido), an arylazo group (e.g., phenylazo, naphthylazo), and a carbamoylamino group (e.g., N-methyl carbamoylamino).

[0026] Preferred of the group that splits off with a nitrogen atom are heterocyclic groups, more preferably aryl heterocyclic groups having 1, 2, 3 or 4 ring-forming nitrogen atoms, or heterocyclic groups represented by the following formula (L):

formula (L)



wherein L represents a moiety that forms a 5- to 6-membered nitrogen-containing heterocycle with the -NC(=O)-.

[0027] Examples of the moieties are enumerated in the explanation of the above-mentioned heterocyclic group, and such moieties as enumerated above are more preferred.

[0028] Particularly preferably L is a moiety that forms a 5-membered nitrogen-containing heterocyclic ring.

[0029] Examples of the group that splits off with an oxygen atom include an aryloxy group (e.g., phenoxy, 1-naphthoxy), a heterocyclic oxy group (e.g., pyridyloxy, pyrazolyloxy), an acyloxy group (e.g., acetoxy, benzoyloxy), an alkoxy group (e.g., methoxy, dodecyloxy), a carbamoyloxy group (e.g., N,N-diethylcarbamoyloxy, morpholinocarbamoyloxy), an aryloxycarbonyloxy group (e.g., phenoxycarbonyloxy), an alkoxycarbonyloxy group (e.g., methoxycarbonyloxy, ethoxycarbonyloxy), an alkylsulfonyloxy group (e.g., methanesulfonyloxy), and an aryl sulfonyloxy group (e.g., benzenesulfonyloxy, toluenesulfonyloxy).

[0030] Preferred of the group that splits off with an oxygen atom are an aryloxy group, an acyloxy group and a heterocyclic oxy group.

[0031] Examples of the group that splits off with a sulfur atom include an arylthio group (e.g., phenylthio, naphthylthio), a heterocyclic thio group (e.g., tetrazolylthio, 1,3,4-thiadiazolylthio, 1,3,4-oxazolylthio, benzimidazolyl thio), an alkylthio group (e.g., methylthio, octylthio, hexadecylthio), an alkylsulfinyl group (e.g., methane sulfinyl), an arylsulfinyl group (e.g., benzenesulfinyl), an arylsulfonyl group (e.g., benzenesulfonyl), and an alkylsulfonyl group (e.g., methansulfonyl).

[0032] Preferred of the group that splits off with a sulfur atom are an arylthio group and a heterocyclic thio group. A heterocyclic thio group is more preferred.

[0033] X may be substituted with a substituent. Examples of the substituent substituting on X include those exemplified as the substituent of the above-mentioned R1.

[0034] X is preferably a group that can split off upon a coupling reaction with an oxidized product of a developing agent. Among such split-off groups, preferred are groups that can split off with a nitrogen atom, groups that can split off with an oxygen atom, and groups that can split off with a sulfur atom. More preferably the split-off group is a group that can split off with a nitrogen atom, and further preferably, the split-off group is one of the above-mentioned preferable examples, and they are preferable in the described order.

[0035] Preferable groups of X are explained in more detail below. The group that can split off with a nitrogen atom is preferable; and an aromatic heterocyclic group having at least two nitrogen atoms (preferably 2) (preferably a 5-membered aromatic heterocyclic group, such as a pyrazole group, optionally having a substituent) and a group represented by the above-mentioned formula (L) are particularly preferable.

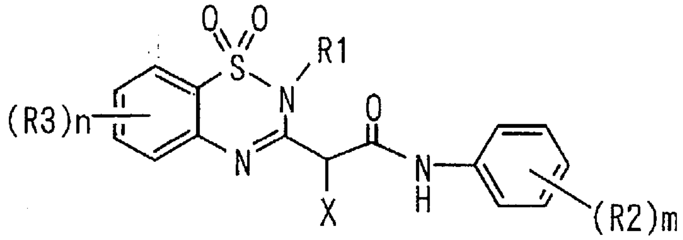
[0036] X may be a photographically useful group. Examples of the photographically useful group include a development inhibitor, a desilvering accelerator, a redox compound, a dye, a coupler, and precursors of these compounds.

[0037] In the present invention, it is preferable that X does not act as the above-mentioned photographically useful group.

[0038] In order to render the coupler immobile in the light-sensitive material, at least one of Q, R1, X and R2 has preferably 8 to 50 carbon atoms, more preferably 10 to 40 carbon atoms in total respectively, including carbon atoms of substituent(s) that they may have.

[0039] It is preferable, from the point of the effects of the present invention, that the compound represented by formula (I) is a compound represented by formula (II). Here, the compound represented by formula (II) is also referred to as a dye-forming coupler. Formula (II) is explained in detail below.

formula (II)



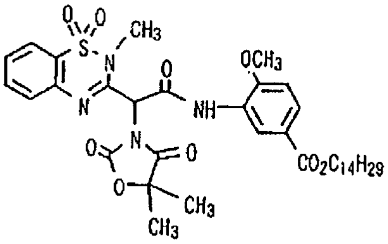
[0040] In formula (II), R1, R2, m, and X each have the same meanings as described in formula (I). Preferable ranges thereof are also the same.

[0041] In formula (II), R3 represents a substituent. Examples of the substituent include those groups and atoms exemplified as the substituent of the above-mentioned R1. Preferably R3 is a halogen atom (i.e., fluorine, chlorine, bromine), an alkyl group (e.g., methyl, isopropyl), an aryl group (e.g., phenyl, naphthyl), an alkoxy group (e.g., methoxy, isopropyloxy), an aryloxy group (e.g., phenoxy), an acyloxy group (e.g., acetyloxy), an amino group (e.g., dimethylamino, morpholino), an acylamino group (e.g., acetoamido), a sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido), an alkoxycarbonyl group (e.g., methoxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), a carbamoyl group (e.g., N-methylcarbamoyl, N,N-diethylcarbamoyl), a sulfamoyl group (e.g., N-methylsulfamoyl, N, N-diethylsulfamoyl), an alkylsulfonyl group (e.g., methane sulfonyl), an arylsulfonyl group (e.g., benzene sulfonyl), a cyano group, a carboxyl group, and a sulfo group.

[0042] n represents an integer of 0 to 4. When n is 2 or more, the multiple R3s may be the same or different, and the R3s may bond each other to form a ring.

[0043] Preferable specific examples of the couplers represented by formula (I) or (II) according to the present invention are shown below. However, the present invention is not limited to these compounds. Herein, the present invention also embraces tautomers, in which the hydrogen atom at the coupling site (the hydrogen atom on the carbon atom to which X is substituting) is transferred on the nitrogen atom in the C=N portion bonding to the coupling site (the ring-constituting nitrogen atom that is not bonded with R1).

(1)



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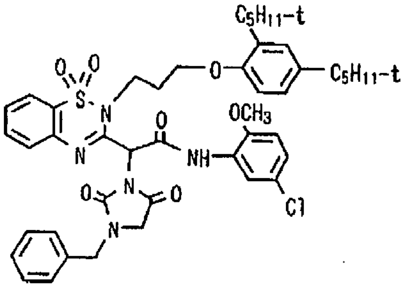

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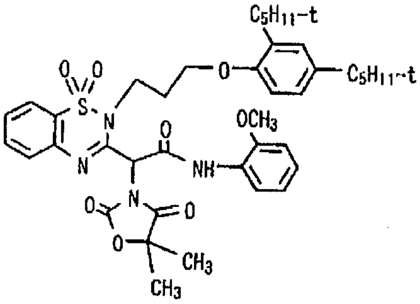

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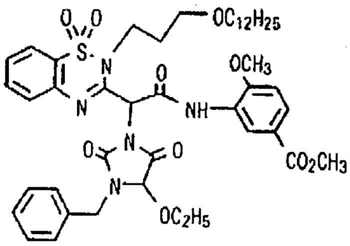

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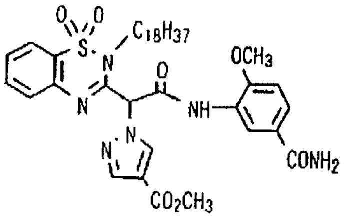

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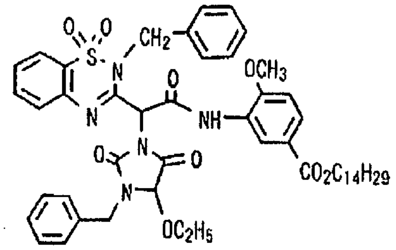

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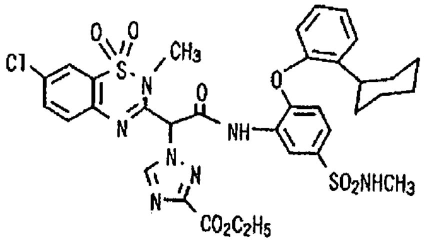

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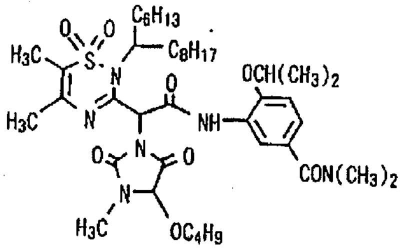

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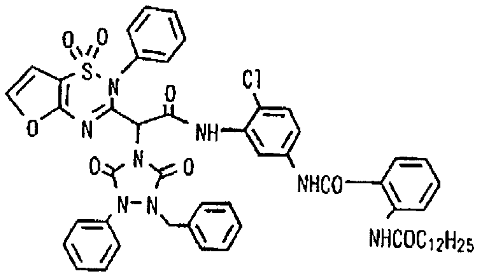

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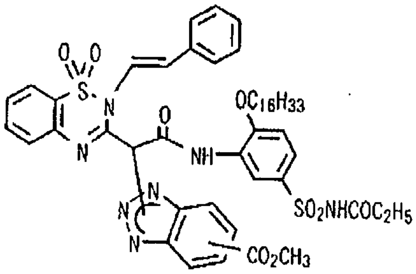

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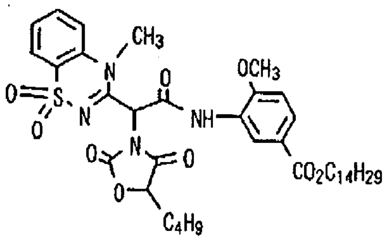

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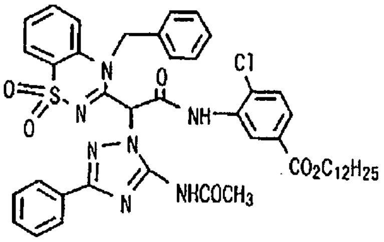

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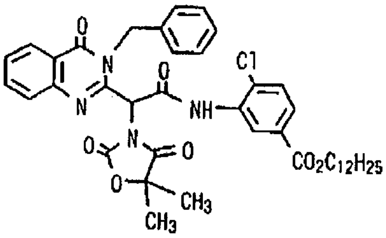

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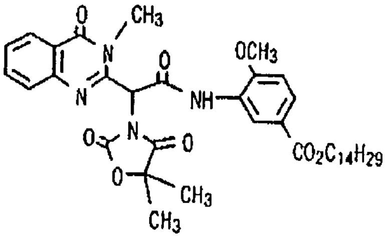

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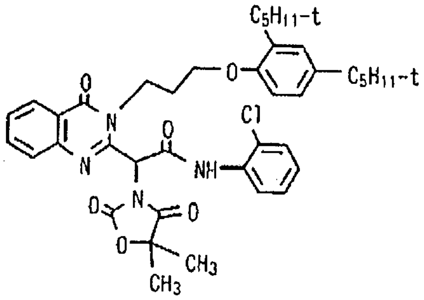

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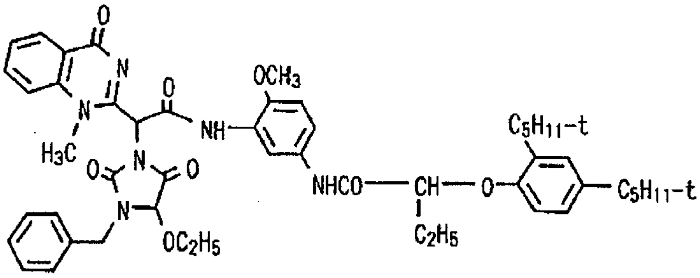

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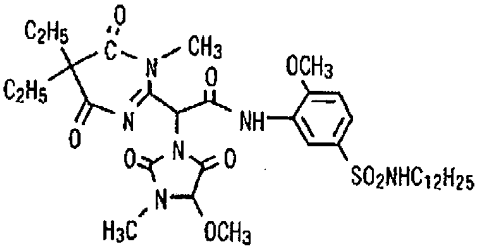

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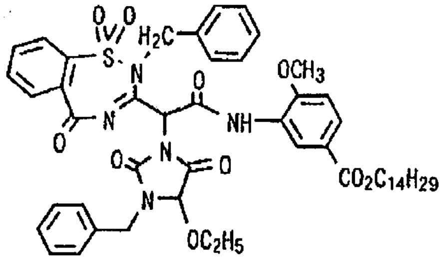

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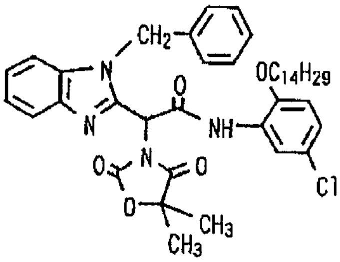

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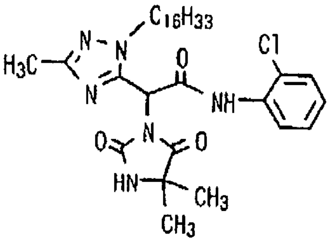

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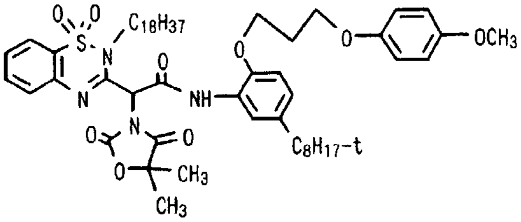

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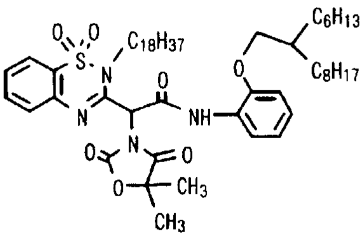
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CH3

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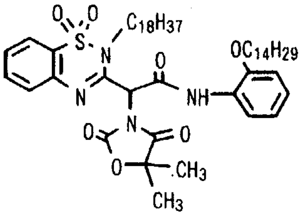
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CH3

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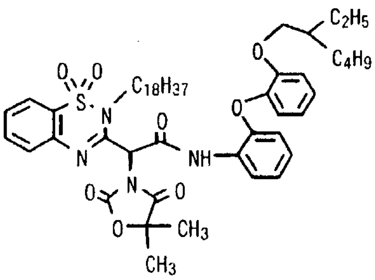
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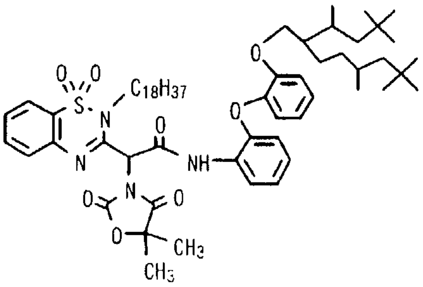
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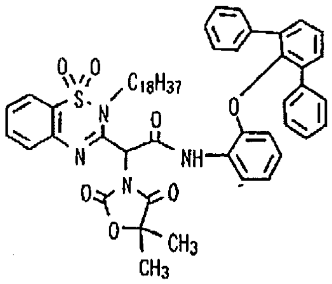
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CH3
CH3

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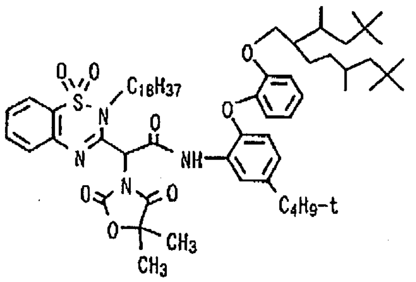
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O
O
C4H9-t
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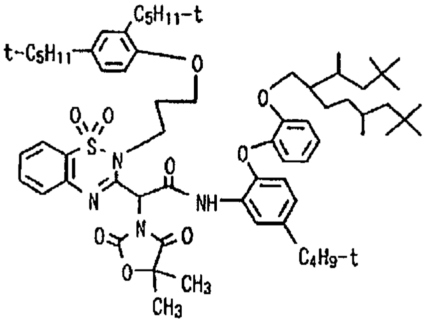
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NH
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CH3

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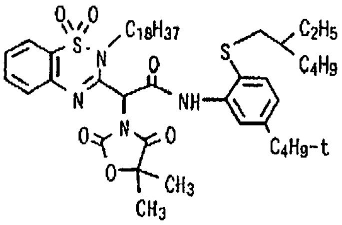
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CH3

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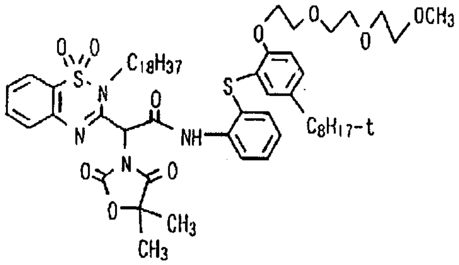
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CH3
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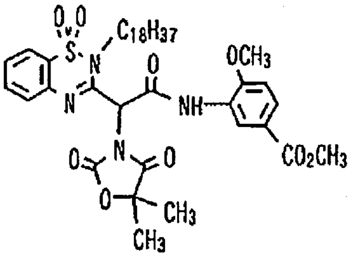

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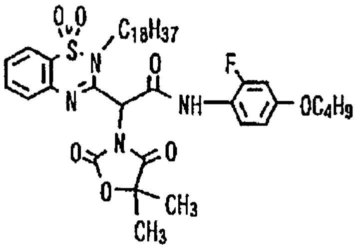

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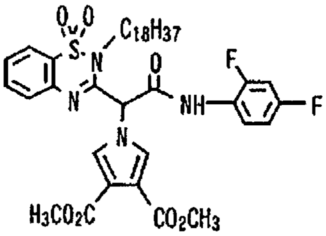

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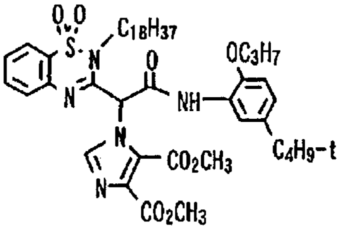

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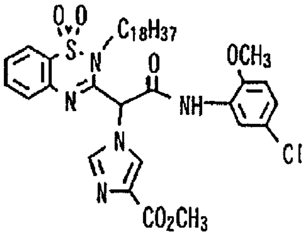
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N
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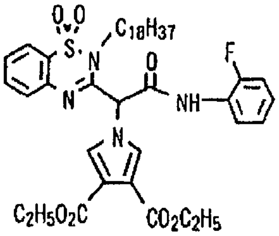
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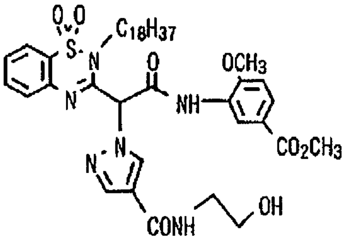
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N
CONH
OH

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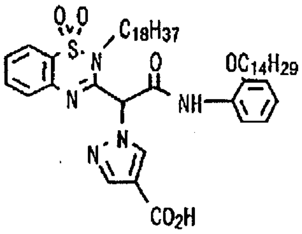
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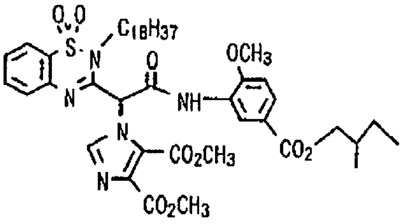

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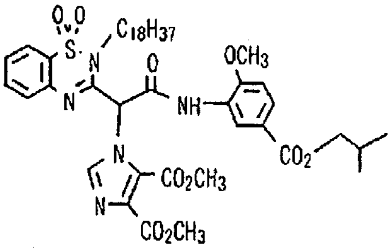

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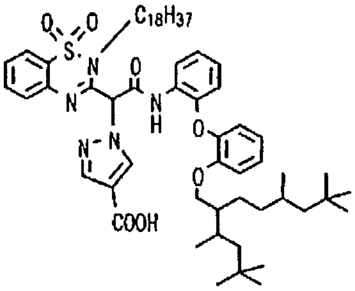

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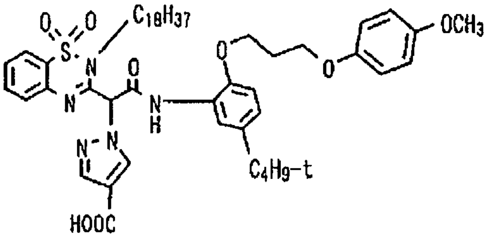

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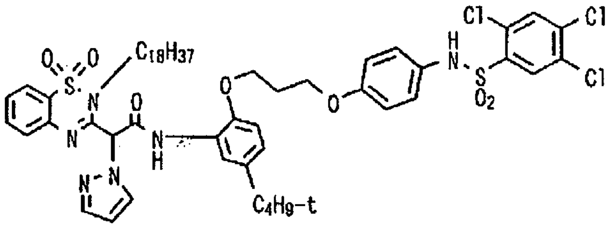

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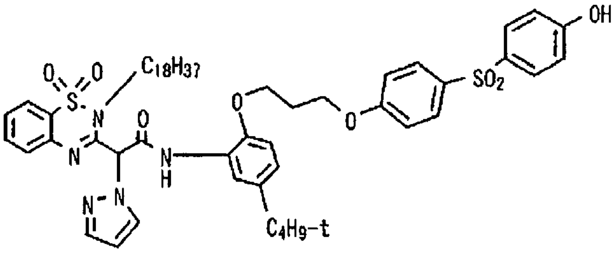

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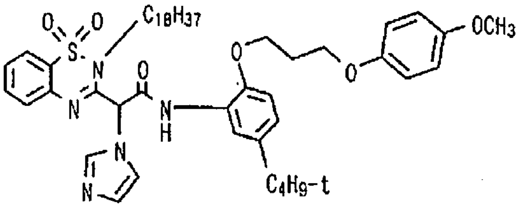

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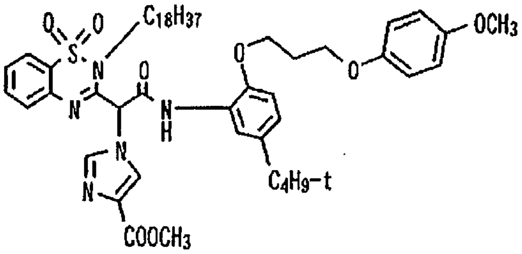

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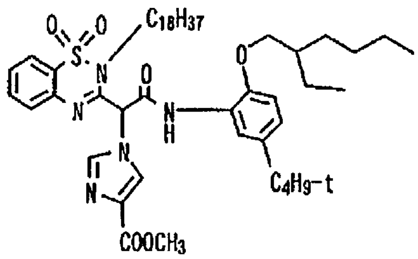

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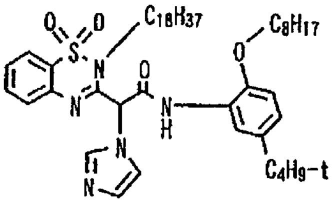

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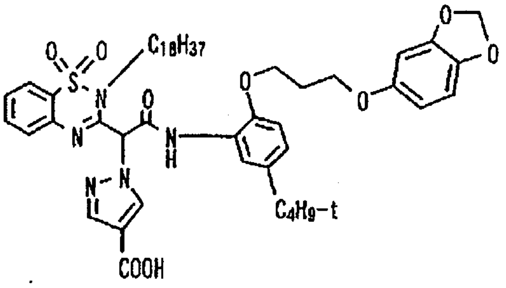

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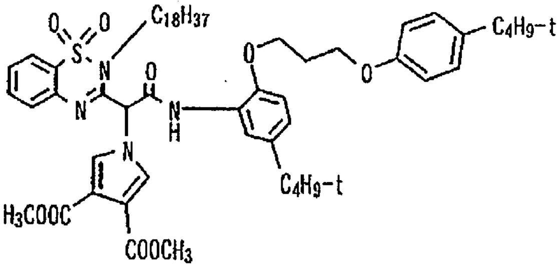
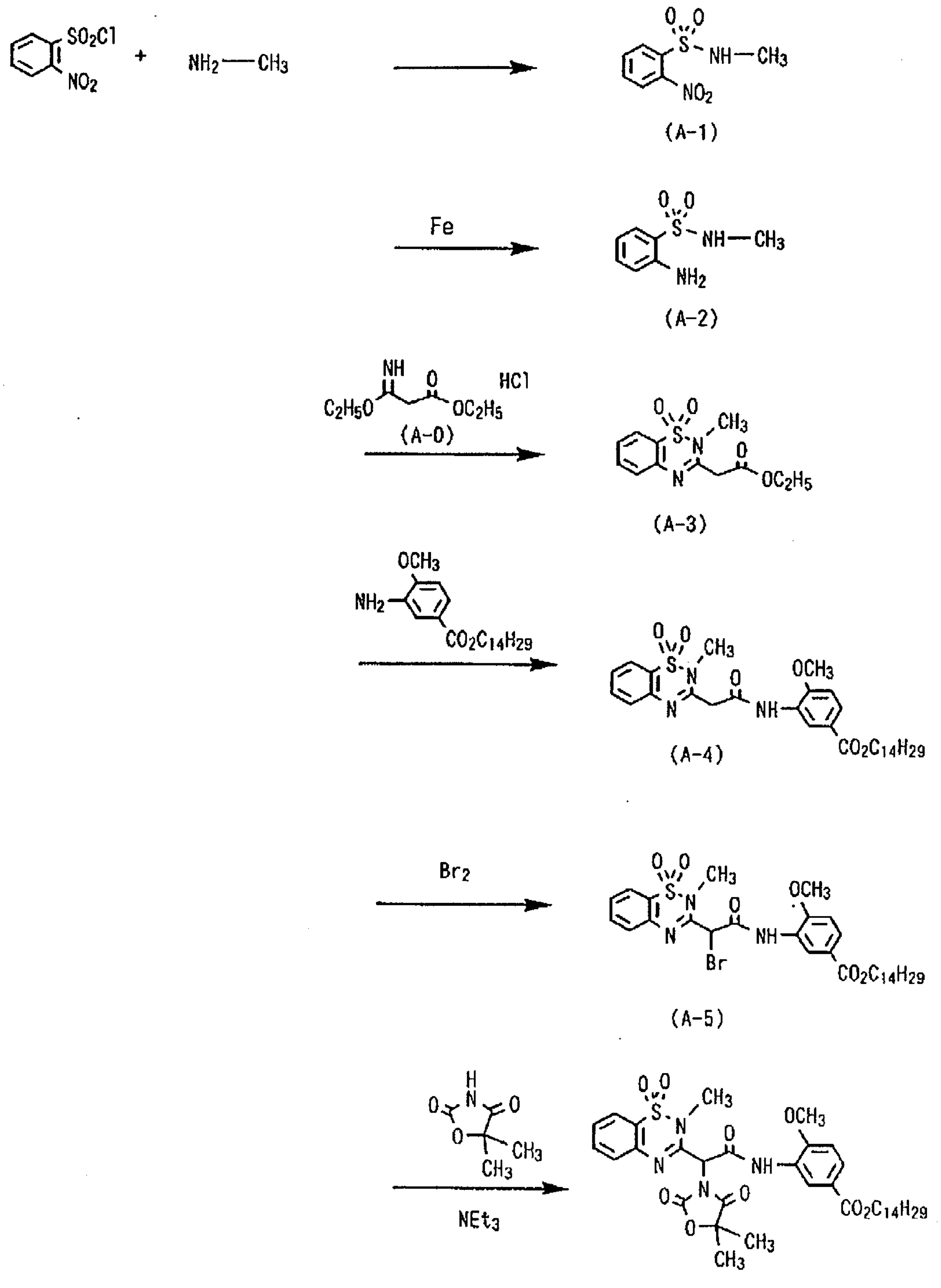


[0044] In the following explanation, when the exemplified compounds (hereinafter also referred to as a dye-forming coupler) shown above are referred to, they are expressed as "coupler (x)", with using the number x labeled to each of the exemplified compounds in the parenthesis.

[0045] Specific synthetic examples of the compounds represented by the foregoing formula (I) or (II) are described below.

Synthetic Example 1: Synthesis of Coupler (1)

[0046] Coupler (1) was synthesized according to the following synthesis route:



Coupler (1)

[0047] 44.3 g of o-nitrobenzenesulfonyl chloride was gradually added, with stirring, to a mixture solution of 38.8g of an aqueous 40% methylamine solution and 200 ml of acetonitrile, on an ice bath. The resulting reaction mixture was heated up to room temperature and stirred for another 1 hour. Thereafter, ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with dilute hydrochloric acid and then a saturated brine. After the organic layer was dried with magnesium sulfate anhydride, the solvent was removed by vacuum distillation. Crystallization from a mixed solvent of ethyl acetate and hexane gave 28.6 g of Compound (A-1).

[0048] 44.8 g of reduced iron and 4.5 g of ammonium chloride were dispersed in a mixture of 270 ml of isopropanol and 45 ml of water, and heated for 1 hour under refluxing. To the resulting mixture, 25.9 g of Compound (A-1) was gradually added with stirring. After heating in refluxing for another 1 hour, insoluble matters were removed by a suction filtration through Celite. Ethyl acetate and water were added to the filtrate, and the organic layer was separated from the aqueous layer. The organic layer was washed with a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation, to yield 21.5 g of Compound (A-2) as an oily product.

[0049] A solution of 18.9 g of Compound (A-2), 39.1 g of hydrochloride of iminoether (A-0) and 200 ml of ethyl alcohol was stirred with heating in refluxing for 1 day. Further, 19.2 g of hydrochloride of iminoether was added and stirred with heating in refluxing for another 1 day. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. Crystallization from a mixed solvent of ethyl acetate and hexane gave 21.0 g of Compound (A-3).

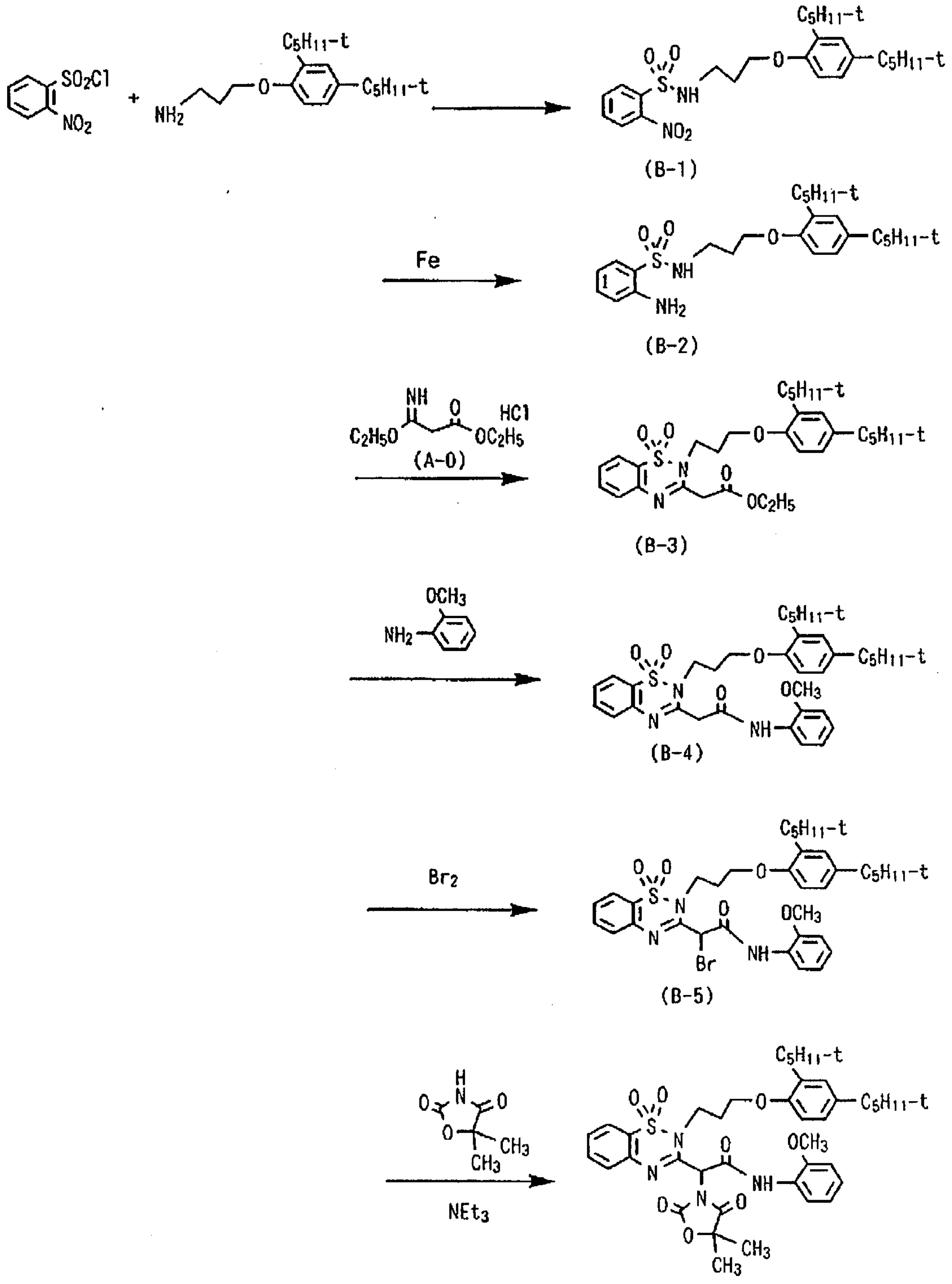
[0050] A solution of 5.6 g of Compound (A-3), 7.2 g of 2-methoxy-5-tetradecyloxycarbonylaniline and 20 ml of m-dichlorobenzene was stirred with heating in refluxing for 6 hours. After cooling, crystallization by adding hexane gave 8.8 g of Compound (A-4).

[0051] To 110 ml of methylene chloride solution containing 5.4 g of Compound (A-4), 10 ml of methylene chloride solution containing 0.45 ml of bromine was added drop-wise on an ice bath. After the resultant mixture was stirred for 30 minutes at room temperature, methylene chloride and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation, to obtain a crude product of Compound (A-5).

[0052] To a solution which was prepared by dissolving 3.5 g of 5,5-dimethyloxazolidine-2,4-dione and 3.8 ml of triethylamine in 110 ml of N,N-dimethyl acetoamide, a solution containing all the previously synthesized crude product of Compound (A-5) dissolved in 25 ml of acetonitrile was added drop-wise over 10 minutes at room temperature, and then stirred for 2 hours at room temperature. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with 0.1 normal aqueous potassium hydroxide solution, dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. The residue was purified on silica gel column chromatography using a mixed solvent of acetone and hexane as an eluate, and then recrystallized from a mixed solvent of ethyl acetate and hexane, to give 4.7 g of Coupler (1).

Synthetic Example 2: Synthesis of Coupler (3)

[0053] Coupler (3) was synthesized according to the following synthesis route:



Coupler (3)

[0054] To a solution containing 438 g of 3-(2,4-di-t-amylphenoxy) propylamine, 210 ml of triethylamine and 1 liter of acetonitrile, 333 g of o-nitrobenzenesulfonyl chloride was gradually added with stirring on an ice bath. The resulting reaction mixture was heated up to room temperature and further stirred for 1 hour. Thereafter, ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with dilute hydrochloric acid and a saturated brine. After the organic layer was dried with magnesium sulfate anhydride, the solvent was removed by vacuum distillation. Crystallization from a mixed solvent of ethyl acetate and hexane gave 588 g of

Compound (B-1).

[0055] 84.0 g of reduced iron and 8.4 g of ammonium chloride were dispersed in a mixture of 540 ml of isopropanol and 90 ml of water, and heated in refluxing for 1 hour. To the resulting dispersion, 119 g of Compound (B-1) was gradually added with stirring. After heating in refluxing for another 2 hours, the reaction mixture was filtrated by a suction filtration through Celite. Ethyl acetate and water were added to the filtrate, and the organic layer was separated from the aqueous layer. The organic layer was washed with a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation, to yield 111 g of Compound (B-2) as an oily product.

[0056] A solution of 111 g of Compound (B-2), 68.4 g of hydrochloride of iminoether (A-0) and 150 ml of ethyl alcohol was stirred with heating in refluxing for 1 hour. Additionally 4.9 g of hydrochloride of iminoether was added and stirred with heating in refluxing for 30 minutes. After cooling the reaction mixture, it was filtered under suction, 100 ml of p-xylene was added to the filtrate and then heated in refluxing for 4 hours while removing ethyl alcohol by distillation. The reaction solution was purified by a silica gel column chromatography using a mixed solvent of ethyl acetate and hexane as the eluate. Crystallization from methanol gave 93.1 g of Compound (B-3).

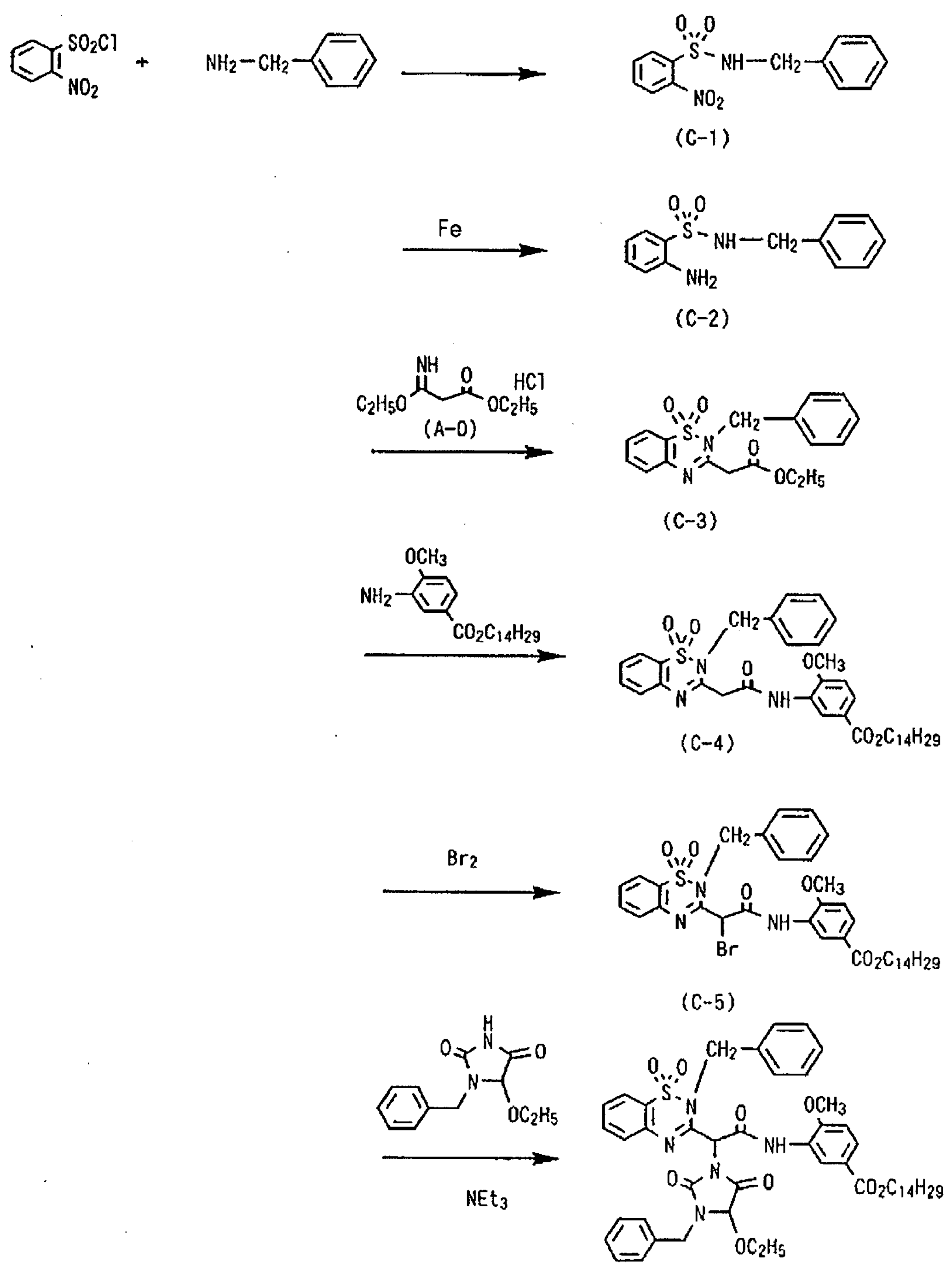
[0057] A solution of 40.7 g of Compound (B-3), 18.5 g of 2-methoxyaniline and 10 ml of p-xylene was stirred with heating in refluxing for 6 hours. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. Purification of the residue by a silica gel column chromatography using a mixed solvent of ethyl acetate and hexane as the eluate gave 37.7 g of Compound (B-4) as an oily product.

[0058] To a solution of 24.8 g of Compound (B-4) in 400 ml of methylene chloride, 35 ml of methylene chloride solution containing 2.1 ml of bromine was added drop-wise on an ice bath. After the mixture was stirred for 30 minutes on an ice bath, methylene chloride and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation, to obtain Compound (B-5) as a crude product.

[0059] To a solution of 15.5 g of 5,5-dimethyl oxazolidine-2,4-dione and 16.8 ml of triethylamine in 200 ml of N,N-dimethyl acetoamide, a solution containing all the previously synthesized crude product of Compound (B-5) dissolved in 40 ml of acetonitrile was added drop-wise over 10 minutes at room temperature. The resultant mixture was heated up to 40 °C and then stirred for 30 minutes. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with 0.1 normal aqueous potassium hydroxide solution, dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. The residue was purified by a silica gel column chromatography using a mixed solvent of acetone and hexane as the eluate. Crystallization from a mixed solvent of ethyl acetate and hexane gave 23.4 g of Coupler (3).

Synthetic Example 3: Synthesis of Coupler (6)

[0060] Coupler (6) was synthesized according to the following synthesis route:



Coupler (6)

[0061] To a solution of 21.4 g of benzylamine in 200 ml of acetonitrile, 39.9 g of o-nitrobenzenesulfonyl chloride was gradually added with stirring on an ice bath. The resulting reaction mixture was heated up to room temperature. Further, 30 ml of triethylamine was added drop-wise and stirred for 1 hour. Thereafter, ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with dilute hydrochloric acid and then a saturated brine. After the organic layer was dried with magnesium sulfate anhydride, the solvent was removed by vacuum distillation. Crystallization from a mixed solvent of ethyl acetate and hexane gave 31.2 g of Compound (C-1).

[0062] 44.8 g of reduced iron and 4.5 g of ammonium chloride were dispersed in a mixture of 270 ml of isopropanol and 45 ml of water, and heated for 1 hour in refluxing. To the resulting mixture, 29.2 g of Compound (C-1) was gradually added with stirring. After heating in refluxing for another 1 hour, the reaction mixture was filtrated by a suction filtration through Celite. Ethyl acetate and water were added to the filtrate, and the organic layer was separated from the aqueous layer. The organic layer was washed with a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation, to yield 25.5 g of Compound (C-2) as an oily product.

[0063] A solution of 19.7 g of Compound (C-2) and 22.0 g of hydrochloride of iminoether (A-0) in 200 ml of ethyl alcohol was stirred with heating in refluxing for 4 hours. Further, 19.7g of hydrochloride of the iminoether was added and stirred with heating under reflux for 4 hours. Additionally 13 g of p-toluene sulfonic acid monohydrate was added and stirred with heating in refluxing for 1 hour. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. Crystallization from a mixed solvent of ethyl acetate and hexane gave 3.2 g of Compound (C-3).

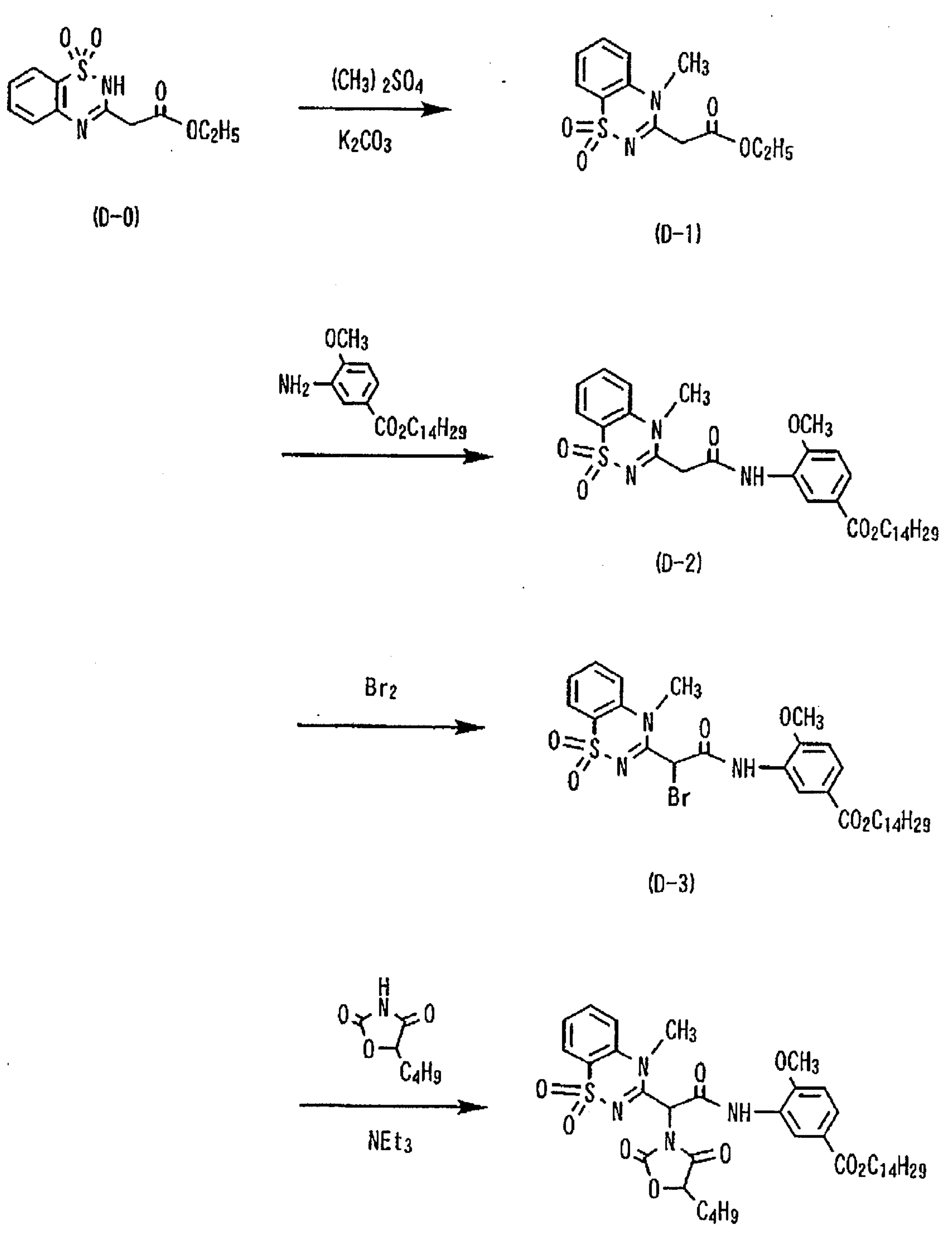
[0064] A solution of 2.9 g of Compound (C-3), 2.9 g of 2-methoxy-5-tetradecyloxycarbonylaniline in 20 ml of o-dichlorobenzene was stirred for 6 hours with heating in refluxing. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. The residue was purified by a silica gel column chromatography using a mixed solvent of ethyl acetate and hexane as the eluate. Crystallization from a mixed solvent of ethyl acetate and hexane gave 3.8 g of Compound (C-4).

[0065] To a solution containing 3.4 g of Compound (C-4) in 100 ml of methylene chloride, 10 ml of methylene chloride solution containing 0.26 ml of bromine was added drop-wise on an ice bath. After the mixture was stirred for 30 minutes at room temperature, methylene chloride and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation, to obtain a crude product of Compound (C-5).

[0066] To a solution of 3.5 g of 1-benzyl-5-ethoxyhydantoin and 2.1 ml of triethylamine in 100 ml of N,N-dimethyl acetoamide, a solution containing all the previously synthesized crude product of Compound (C-5) dissolved in 20 ml of acetonitrile was added drop-wise over 30 minutes at room temperature, and then stirred at 40 °C for 2 hours. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with 0.1 normal aqueous potassium hydroxide solution, dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. The residue was purified by a silica gel column chromatography using a mixed solvent of ethyl acetate and hexane as the eluate. Crystallization from a mixed solvent of ethyl acetate and hexane gave 3.0 g of Coupler (6).

Synthetic Example 4: Synthesis of Coupler (11)

[0067] Coupler (11) was synthesized according to the following synthesis route:



Coupler (11)

[0068] To a solution of 26.8 g of Compound (D-0) (Coupler-I described in U.S. Patent No. 3,841,880) and 16.6 g of potassium carbonate in 300 ml of acetone, 13.9 g of dimethyl sulfate was added drop-wise and stirred for 2 hours with heating in refluxing. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. The residue was purified by a silica gel column chromatography using a mixed solvent of acetone and hexane as the eluate. Crystallization from a mixed solvent of ethyl acetate and hexane gave 5.6 g of Compound (D-1). At the same time, 10.9 g of Compound (A-3) was obtained as a by-product. Coupler (1) may be synthesized using Compound (A-3) thus prepared.

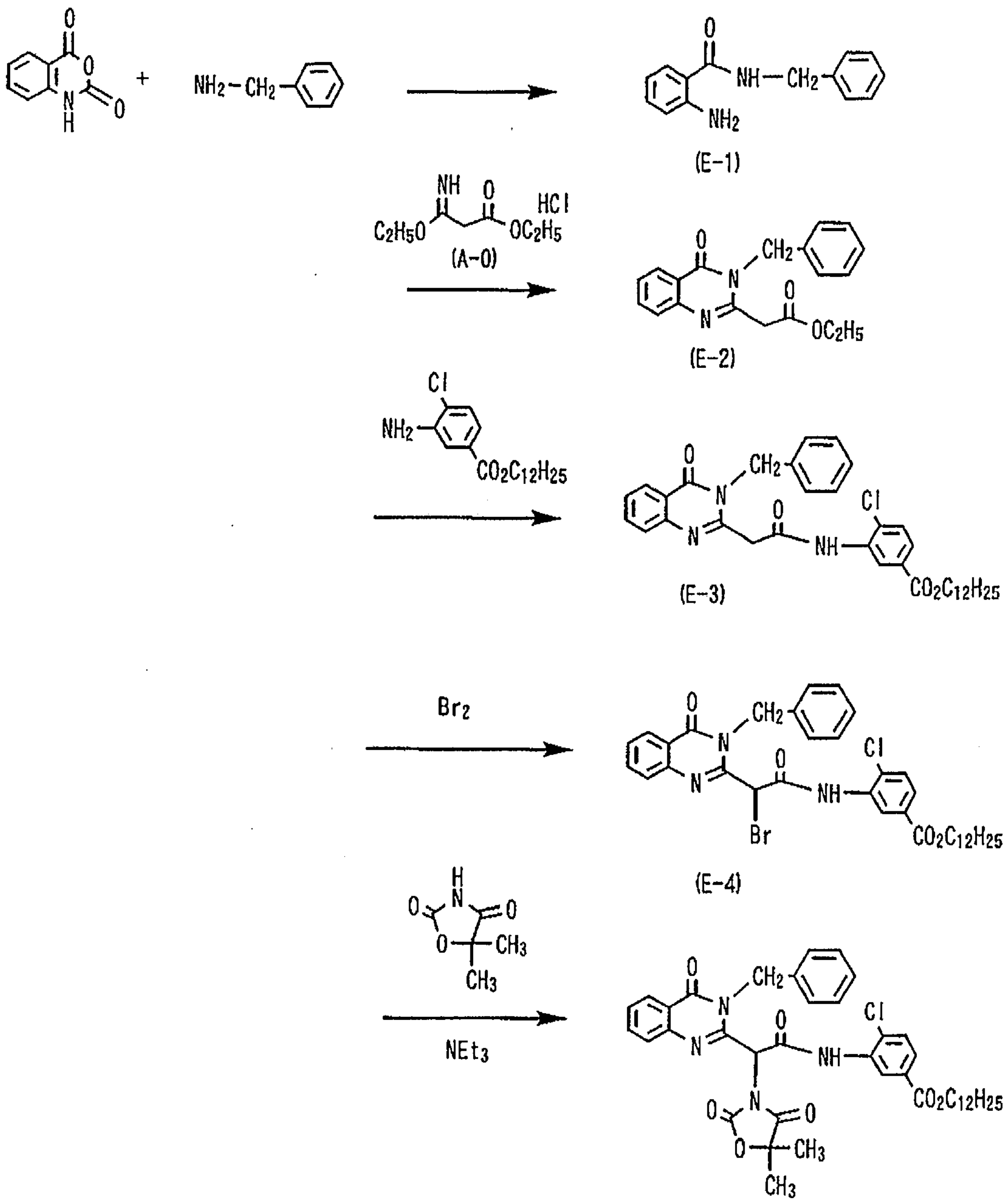
[0069] A solution of 5.4 g of Compound (D-1) and 7.3 g of 2-methoxy-5-tetradecyloxycarbonylaniline in 50 ml of o-dichlorobenzene was stirred for 6 hours with heating in refluxing. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. Crystallization from a mixed solvent of ethyl acetate and methanol gave 9.1 g of Compound (D-2).

[0070] To a solution of 4.8 g of Compound (D-2) in 100 ml of methylene chloride, 10 ml of a methylene chloride solution containing 0.4 ml of bromine was added drop-wise on an ice bath. The reaction mixture was stirred for 30 minutes on an ice bath. Thereafter, methylene chloride and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation, to obtain a crude product of Compound (D-3).

[0071] To a solution of 3.8 g of 5-butyloxazolidine-2,4-dione and 3.4 ml of triethylamine dissolved in 100 ml of N,N-dimethyl acetamide, a solution containing all the previously synthesized crude product of Compound (D-3) dissolved in 50 ml of N,N-dimethylacetamide was added drop-wise at room temperature over 30 minutes, and the resultant mixture was stirred for 1 hour at room temperature. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with 0.1 normal aqueous potassium hydroxide solution, dilute hydrochloric acid and a saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. The residue was purified by a silica gel column chromatography using a mixed solvent of acetone, tetrahydrofuran, and hexane as the eluate. Crystallization from a mixed solvent of ethyl acetate and hexane gave 2.1 g of Coupler (11).

Synthetic Example 5: Synthesis of Coupler (13)

[0072] Coupler (13) was synthesized in the synthesis route shown below.



Coupler (13)

[0073] 32.2 g of benzylamine was added, drop-wise, to 200 ml of an acetonitrile solution containing 48.9 g of isatoic acid anhydride, and the resulting mixture was stirred. The resulting mixture was heated up to 60 °C and further stirred for 10 minutes. Thereafter, ethyl acetate and water were added thereto, and the organic layer was separated from the aqueous layer. The organic layer was dried with magnesium sulfate anhydride, and then the solvent was removed by vacuum distillation. Crystallization from a mixed solvent of ether and hexane gave 54.6 g of Compound (E-1).

[0074] 200 ml of an ethyl alcohol solution containing 24.9 g of Compound (E-1), 21.6 g of hydrochloride of iminoether (A-0) and 10.5 g of paratoluenesulfonic acid monohydrate was stirred for 3 hours with heating under reflux. After cooling, 21.6 g of hydrochloride of iminoether was added and further stirred with heating under reflux for 1 hour. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. Crystallization from a mixed solvent of ether and hexane gave 33.6 g of Compound (E-2).

[0075] 50 ml of p-xylene solution containing 6.5 g of Compound (E-2) and 6.5 g of 2-chloro-5-dodecyloxycarbonylaniline was stirred for 2 hours with heating under reflux. Further, 0.2 g of p-toluenesulfonic acid monohydrate was added and stirred for 4 hours with heating under reflux. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with 1-normal aqueous solution of hydrochloric acid and saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. Crystallization from a mixed solvent of ethyl acetate and hexane gave 6.7 g of Compound (E-3).

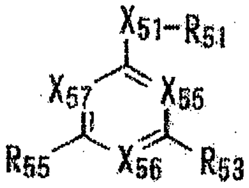
[0076] To 70 ml of a methylene chloride solution containing 5.5 g of Compound (E-3), 15 ml of a methylene chloride solution containing 0.48 ml of bromine was added drop-wise under cooling with ice. After the mixture was stirred at room temperature for 30 minutes, methylene chloride and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation, to obtain a crude product of Compound (E-4).

[0077] To a solution which was prepared by dissolving 3.5 g of 5-dimethyloxazolidine-2,4-dione and 3.8 ml of triethylamine in 50 ml of N,N-dimethyl acetoamide, a solution containing all the previously synthesized crude product of Compound (E-4) dissolved in 50 ml of N,N-dimethyl acetoamide, was added drop-wise over 10 minutes at room temperature, and then stirred for 1 hour at room temperature. Ethyl acetate and water were added, and the organic layer was separated from the aqueous layer. The organic layer was washed with 1 normal aqueous solution of potassium carbonate, 1 normal aqueous solution of hydrochloric acid and saturated brine, and then dried with magnesium sulfate anhydride. The solvent was removed by vacuum distillation. Purification of the residue by silica gel column chromatography using a mixed solvent of ethyl acetate and hexane as the eluate gave 4.0 g of Coupler (13) as an amorphous product.

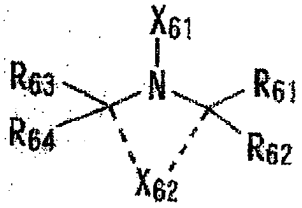
[0078] The dye-forming coupler represented by formula (I) or (II) is added in an amount preferably 1 x 10^{-3} mole or more, more preferably 1 x 10^{-3} to 1 mole, and further preferably 2 x 10^{-3} to 3 x 10^{-1} mole, per mol of silver halide.

[0079] Next, the compound represented by any one of the formulae (TS-I), (TS-II), (TS-III), (TS-IV), (TS-V), and (TS-VI), and the metal complex, for use in the present invention are explained in detail.

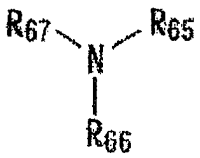
formula (TS-I)



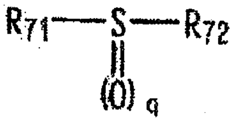
formula (TS-II)



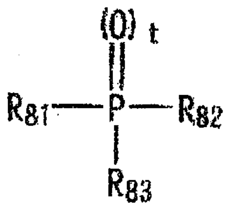
formula (TS-III)



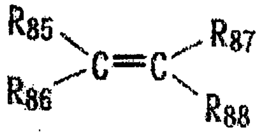
formula (TS-IV)



formula (TS-V)



formula (TS-VI)



[0080] The compound represented by formula (TS-I) is described in more detail.

[0081] R_{51} represents a hydrogen atom, an aliphatic group (e.g., methyl, i-propyl, s-butyl, dodecyl, methoxyethyl, allyl, benzyl), an aryl group (e.g., phenyl, p-methoxyphenyl), a heterocyclic group (e.g., 2-tetrahydrofuryl, pyranyl), an acyl group (e.g., acetyl, pivaroyl, benzoyl, acryloyl), an aliphatic oxycarbonyl group (e.g., methoxycarbonyl, hexadecyloxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl, p-methoxy phenoxycarbonyl), an aliphatic sulfonyl group (e.g., methane sulfonyl, butane sulfonyl), an aryl sulfonyl group (e.g., benzene sulfonyl, p-toluene sulfonyl), a phosphoryl group (e.g., diethyl phosphoryl, diphenyl phosphoryl, diphenoxy phosphoryl), or -Si(R_{58}) (R_{59}) (R_{60}).

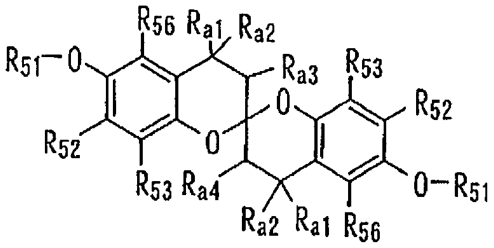
[0082] Herein, R_{58}, R_{59}, and R_{60} each independently represent an aliphatic group (e.g., methyl, ethyl, t-butyl, benzyl, allyl), an aryl group (e.g., phenyl), an aliphatic oxy group (e.g., methoxy, butoxy), or an aryloxy group (e.g., phenoxy). X_{51} represents -O- or -N(R_{57})-, in which R_{57} has the same meaning as R_{51}. X_{55} represents -N= or -C(R_{52})=, X_{56} represents -N= or -C(R_{54})=, X_{57} represents -N= or -C(R_{56})=. R_{52}, R_{53}, R_{54}, R_{55}, and R_{56} each independently represent a hydrogen atom, or a substituent. As the preferable substituent exemplified are an aliphatic group (e.g., methyl, t-butyl, t-hexyl, benzyl), an aryl group (e.g., phenyl), an aliphatic oxycarbonyl group (e.g., methoxycarbonyl, dodecyloxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), an aliphatic sulfonyl group (e.g., methane sulfonyl, butane sulfonyl), an aryl sulfonyl group (e.g., benzene sulfonyl, p-hydroxy benzene sulfonyl), and $-X_{51}-R_{51}$.

[0083] Each combination of R_{51} and R_{52}, R_{57} and R_{56}, and R_{51} and R_{57} may combine together to form a 5- to 7-membered ring (such as a chroman ring and a morpholine ring). Further, each combination of R_{52} and R_{53}, and R_{53} and R_{54} may combine together to form a 5- to 7-membered ring (such as a chroman ring and an indan ring), a spiro ring, or a bicycro ring. However, all of R_{51} to R_{57} simultaneously are not a hydrogen atom, and the total number of carbon atoms in each of these groups is generally 10 or more (preferably 10 to 50), and more preferably 16 or more (preferably 16 to 40). Further, in formula (I), when a 4-pyrimidone ring is formed with Q, and R1 is an alkyl group having 1 to 6 carbon atoms, any one of X_{55}, X_{56} and X_{57} is -N=.

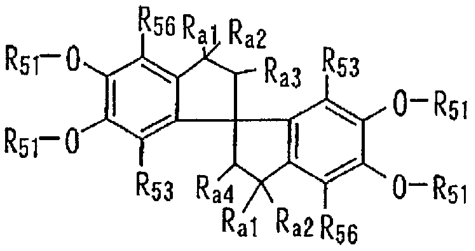
[0084] The compound represented by formula (TS-I) for use in the present invention include those compounds represented by, for example, formula (I) of JP-B-63-50691 ("JP-B" means examined Japanese patent publication), formula (IIIa), (IIIb), or (IIIc) of JP-B-2-37575, formula of JP-B-2-50457, formula of JP-B-5-67220, formula (IX) of JP-B-5-70809, formula of JP-B-6-19534, formula (I) of JP-A-62-227889, formula (I) or (II) of JP-A-62-244046, formula (I) or (II) of JP-A-2-66541, formula (II) or (III) of JP-A-2-139544, formula (I) of JP-A-2-194062, formula (B), (C), or (D) of JP-A-2-212836, formula (III) of JP-A-3-200758, formula (II) or (III) of JP-A-3-48845, formula (B), (C), or (D) of JP-A-3-266836, formula (I) of JP-A-3-969440, formula (I) of JP-A-4-330440, formula (I) of JP-A-5-297541, formula of JP-A-6-130602, formula (1), (2), or (3) of International Patent Application Publication WO 91/11749, formula (I) of German Patent Publication DE4,008,785A1, formula (II) of U.S. Patent No. 4,931,382, formula (a) of European Patent Publication EP203,746B1, formula (I) of European Patent Publication EP264,730B1, and formula (III) of JP-A-62-89962. These compounds can be synthesized according to the method described in these publications or general methods described in Shin Jikken Kagaku Koza, Vol. 14 (Maruzen Co., Ltd.) (1977, 1978).

[0085] From the point of the effects of the present invention, the compounds represented by formula (TS-I) are preferably those compounds represented by any one of formulae (TS-IA), (TS-IB), (TS-IC), (TS-ID), (TS-IE), (TS-IF), (TS-IG), and (TS-IH) shown below.

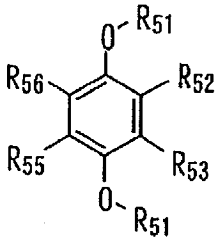
formula (TS-I A)



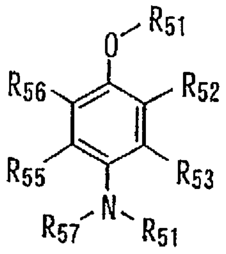
formula (TS-I B)



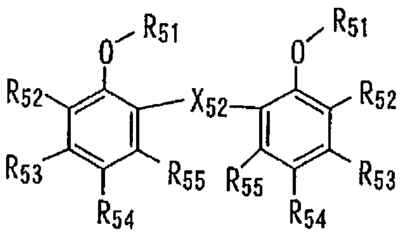
formula (TS-I C)



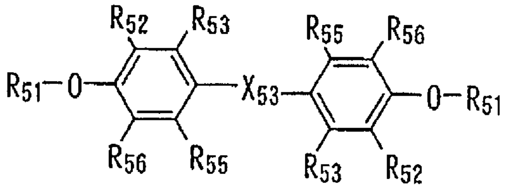
formula (TS-I D)



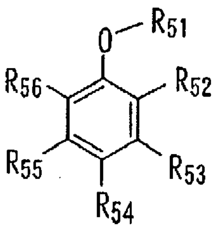
formula (TS-I E)



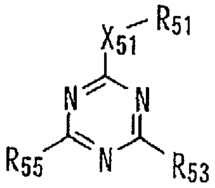
formula (TS-I F)



formula (TS-I G)



formula (TS-I H)



[0086] In formulae (TS-IA) to (TS-IH), R_{51}, R_{52}, R_{53}, R_{54}, R_{55}, R_{56}, and R_{57} have the same meanings as those defined in formula (TS-I). R_{a1}, R_{a2}, R_{a3}, and R_{a4} each represent a hydrogen atom or an aliphatic group (such as methyl and ethyl), and X_{52} and X_{53} each independently represent a divalent linking group. Examples of the divalent linking group include an alkylene group, an oxy group, and a sulfonyl group. In the formulae, the same symbols in the same molecule may be the same or different in meanings.

[0087] As to the compounds represented by any one of formulae (TS-IA) to (TS-IH), substituents preferable in view of the effects of the present invention are described below.

[0088] In formulae (TS-IA), (TS-IB), (TS-IC) and (TS-ID), preferable is the case where R_{51} is a hydrogen atom, an aliphatic group, an acyl group, an aliphatic oxycarbonyl group, an aryl oxycarbonyl group, or a phosphoryl group, and R_{52}, R_{53}, R_{55}, and R_{56} each independently are a hydrogen atom, an aliphatic group, an aliphatic oxy group, or an acyl amino group. More preferable is the case where R_{51} is an aliphatic group, and R_{52}, R_{53}, R_{55}, and R_{56} may be the same or different, and each independently are a hydrogen atom, or an aliphatic group. In formulae (TS-IE), (TS-IF), and (TS-IG), preferable is the case where R_{51} is a hydrogen atom, an aliphatic group, an acyl group, an aliphatic oxycarbonyl group, an aryl oxycarbonyl group, or a phosphoryl group, and R_{52}, R_{53}, R_{55}, and R_{56} each independently are a hydrogen atom, an aliphatic group, an aliphatic oxy group, or an acyl amino group, and R_{54} is an aliphatic group, a carbamoyl group, or an acyl amino group, and X_{52} and X_{53} each independently are an alkylene group or an oxy group. More preferable is the case where R_{51} is a hydrogen atom, an aliphatic group, an acyl group, or a phosphoryl group, and R_{52}, R_{53}, R_{55}, and R_{56} may be the same or different, and each independently are a hydrogen atom, an aliphatic group, an aliphatic oxy group, or an acyl amino group, and R_{54} is an aliphatic group, or a carbamoyl group, and X_{52} and X_{53} each independently are $-CHR_{58}-$ (R_{58} is an alkyl group). In formula (TS-IH), preferable is the case where R_{51} is an aliphatic group, an aryl group, or a heterocyclic group, and R_{53} and R_{55} each independently are an aliphatic oxy group, an aryloxy group, or a heterocyclic oxy group. More preferable is the case where R_{51} is an aryl group, or a heterocyclic group, and R_{53} and R_{55} each independently are an aryloxy group, or a heterocyclic oxy group.

[0089] From the point of the effects of the present invention, the compounds represented by formula (TS-I) are preferably those compounds represented by any one of formulae (TS-IA), (TS-IB), (TS-IC), (TS-IE), and (TS-IG), and most preferably those compounds represented by any one of formulae (TS-IB) and (TS-IE).

[0090] The compound represented by formula (TS-II) is described in detail below.

[0091] In formula (TS-II), R_{61}, R_{62}, R_{63}, and R_{64} each independently are a hydrogen atom, or an aliphatic group (e. g., methyl, ethyl, preferably an alkyl group), X_{61} represents a hydrogen atom, an aliphatic group (e.g., methyl, ethyl, allyl), an aliphatic oxy group (e.g., methoxy, octyloxy, cyclohexyloxy), an aliphatic oxycarbonyl group (e.g., methoxycarbonyl, hexadecyl oxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl, p-chlorophenoxycarbonyl), an acyl group (e.g., acetyl, pivaloyl, methacryloyl), an acyloxy group (e.g., acetoxy, benzoyloxy), an aliphatic oxycarbonyloxy group (e.g., methoxycarbonyloxy, octyloxycarbonyloxy), an aryloxycarbonyloxy group (e.g., phenoxycarbonyloxy), an aliphatic sulfonyl group (e.g., methane sulfonyl, butane sulfonyl), an aryl sulfonyl group (e.g., benzene sulfonyl, p-toluene sulfonyl), an aliphatic sulfinyl group (e.g., methane sulfinyl, octane sulfinyl), an arylsulfinyl group (e.g., benzene sulfinyl, p-toluene sulfinyl), a sulfamoyl group (e.g., dimethylsulfamoyl), a carbamoyl group (e.g., dimethylcarbamoyl, diethylcarbamoyl), a hydroxyl group, or an oxy radical group. X_{62} represents a group of non-metal atoms necessary to form a 5- to 7-membered ring (e.g., piperidine ring, piperazine ring). Provided that, when, in formula (I), 4-pyrimidone ring is formed by Q, and R1 is an alkyl group having 1 to 6 carbon atoms, X_{61} represents a hydrogen atom, an aliphatic group, an aliphatic oxy group, an aliphatic oxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, an aliphatic oxycarbonyloxy group, an aryloxycarbonyloxy group, an aliphatic sulfonyl group, an arylsulfonyl group, an aliphatic sulfinyl group, an arylsulfinyl group, a sulfamoyl group, a carbamoyl group, a hydroxyl group, or an oxy radical group.

[0092] The compound represented by formula (TS-II) for use in the present invention include those compounds represented by, for example, formula (I) of JP-B-2-32298, formula (I) of JP-B-3-39296, formula of JP-B-3-40373, formula (I) of JP-A-2-49762, formula (II) of JP-A-2-208653, formula (III) of JP-A-2-217845, formula (B) of U.S. Patent No. 4,906,555, formula of European Patent Publication EP309,400A2, formula of European Patent Publication EP309,401A1, and formula of European Patent Publication EP309,402A1. These compounds can be synthesized according to the method described in these publications or general methods described in Shin Jikken Kagaku Koza, Vol. 14 (Maruzen Co., Ltd.) (1977, 1978).

[0093] As to the compound represented by formula (TS-II), substituents preferable from the point of the effects of the present invention are described below. From the point of the effects of the present invention, R_{61}, R_{62}, R_{63}, and R_{64} are each preferably an aliphatic group, and more preferably a methyl group. From the point of the effects of the present invention, X_{61} is preferably a hydrogen atom, an aliphatic group, an aliphatic oxy group, an acyl group, an acyloxy group, or an oxyradical group; more preferably a hydrogen atom, an aliphatic group, an aliphatic oxy group, an acyl group, or an oxyradical group; and most preferably an aliphatic group, or an aliphatic oxy group. From the point of the effects of the present invention, X_{62} forms preferably a 6-membered ring, more preferably a piperidine ring. From the point of the effects of the present invention, the compound represented by formula (TS-II) is preferably in an embodiment where R_{61}, R_{62}, R_{63}, and R_{64} each are a methyl group, X_{61} is a hydrogen atom, an aliphatic group, an aliphatic oxy group, an acyl group, or an oxy radical group, and X_{62} forms a 6-membered ring; and more preferably in an embodiment where R_{61}, R_{62}, R_{63}, and R_{64} each are a methyl group, X_{61} is an aliphatic group, or an aliphatic oxy group, and X_{62} forms a piperidine ring.

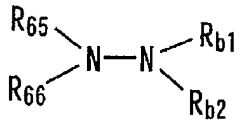
[0094] The compound represented by formula (TS-III) is described in more detail below.

[0095] In formula (TS-III), R_{65} and R_{66} each independently represent a hydrogen atom, an aliphatic group (e.g., methyl, ethyl, t-butyl, octyl, methoxyethyl), an aryl group (e.g., phenyl, 4-methoxyphenyl), an acyl group (e.g., acetyl, pivaloyl, methacryloyl), an aliphatic oxycarbonyl group (e.g., methoxycarbonyl, hexadecyl oxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), a carbamoyl group (e.g., dimethylcarbamoyl, phenylcarbamoyl), an aliphatic sulfonyl group (e.g., methane sulfonyl, butane sulfonyl), or an aryl sulfonyl group (e.g., benzene sulfonyl). R_{67} represents a hydrogen atom, an aliphatic group (e.g., methyl, ethyl, t-butyl, octyl, methoxyethyl), an aliphatic oxy group (e. g., methoxy, octyloxy), an aryloxy group (e.g., phenoxy, p-methoxyphenoxy), an aliphatic thio group (e.g., methylthio, octylthio), an arylthio group (e.g., phenylthio, p-methoxyphenylthio), an acyloxy group (e.g., acetoxy, pivaloyloxy), an aliphatic oxycarbonyloxy group (e.g., methoxycarbonyloxy, octyloxycarbonyloxy), an aryloxycarbonyloxy group (e.g., phenoxycarbonyl oxy), a substituted amino group (the substituent may be any one that is able to substitute for other groups or atoms, e.g., amino groups substituted with a substituent such as an aliphatic group, an aryl group, an acyl group, an aliphatic sulfonyl group or an arylsulfonyl group), a heterocyclic group (e.g., a piperidine ring, a thiomorpholine ring), or a hydroxyl group. If possible, each combination of R_{65} and R_{66}, R_{66} and R_{67}, and R_{65} and R_{67} combine together to form a 5- to 7-membered ring (e.g. a morpholine ring and a pyrazolidine ring), but they never form a 2,2,6,6-tetraalkylpiperidine ring. In addition, both R_{65} and R_{66} simultaneously are not a hydrogen atom. Further, the total number of carbon atoms of R_{65} and R_{66} is 7 or more (preferably 7 to 50).

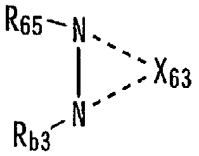
[0096] The compound represented by formula (TS-III) for use in the present invention include those compounds represented by, for example, formula (I) of JP-B-6-97332, formula (I) of JP-B-6-97334, formula (I) of JP-A-2-148037, formula (I) of JP-A-2-150841, formula (I) of JP-A-2-181145, formula (I) of JP-A-3-266836, formula (IV) of JP-A-4-350854 and formula (I) of JP-A-5-61166. These compounds can be synthesized according to the method described in these publications or general methods described in Shin Jikken Kagaku Koza, Vol. 14 (Maruzen Co., Ltd.) (1977, 1978).

[0097] From the point of the effects of the present invention, the compounds represented by formula (TS-III) are preferably those compounds represented by any one of formulae (TS-IIIA), (TS-IIIB), (TS-IIIC), and (TS-IIID).

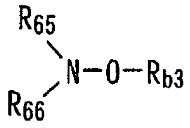
formula (TS-IIIA)



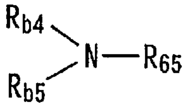
formula (TS-IIIB)



formula (TS-IIIC)



formula (TS-IIID)



[0098] In formulae (TS-IIIA) to (TS-IIID), R_{65} and R_{66} each have the same meanings as those defined in formula (TS-III). R_{b1}, R_{b2}, R_{b3}, and R_{b5} each independently have the same meaning as R_{65}. R_{b4} represents a hydrogen atom, an aliphatic group (e.g., octyl, dodecyl, 3-phenoxypropyl), or an aryl group (e.g., phenyl, 4-dodecyloxyphenyl). X_{63} represents a group of non-metal atoms necessary to form a 5- to 7-membered ring, such as a pyrazolidine ring and a pyrazoline ring.

[0099] As to the compounds represented by any one of formulae (TS-IIIA) to (TS-IIID), substituents preferable from the point of the effects of the present invention are described below. In formula (TS-IIIA), preferable is the case where R_{65} and R_{b1} each independently represent a hydrogen atom, an aliphatic group, or an aryl group, and R_{66} and R_{b2} each independently represent an aliphatic group, an aryl group, or an acyl group; and more preferable is the case where R_{65} and R_{b1} each independently represent an aliphatic group, and R_{66} and R_{b2} each independently represent an aliphatic group, an aryl group, or an acyl group. In formula (TS-IIIB), preferable is the case where R_{65} represents a hydrogen atom, an aliphatic group, an aryl group, an acyl group, or an aliphatic oxycarbonyl group, R_{b3} represents an aliphatic group, an aryl group, or an acyl group, and X_{63} represents a group of non-metal atoms necessary to form a 5-membered ring; and more preferable is the case where R_{65} represents a hydrogen atom, or an aliphatic group, and R_{b3} represents an aliphatic group, or an aryl group, and X_{63} represents a group of non-metal atoms that forms a pyrazolidine ring. In formula (TS-IIIC), preferable is the case where R_{65} and R_{66} each independently represent a hydrogen atom, an aliphatic group, an aryl group, an acyl group, an aliphatic oxycarbonyl group, or an aryl oxycarbonyl group, and R_{b3} represents a hydrogen atom, an aliphatic group, or an acyl group; and more preferable is the case where R_{65} and R_{66} each independently represent an aliphatic group, an acyl group, or an aliphatic oxycarbonyl group, and R_{b3} represents a hydrogen atom, an aliphatic group, or an aryl group. In formula (TS-IIID), preferable is the case where R_{65} represents a hydrogen atom, an aliphatic group, an aryl group, an acyl group, or a carbamoyl group, R_{b5} represents an aliphatic group, or an aryl group, and R_{b4} represents an aliphatic group, or an aryl group; and more preferable is the case where R_{65} represents an aliphatic group, an aryl group, an acyl group, or a carbamoyl group, R_{b5} represents an aliphatic group, or an aryl group, and R_{b4} represents an aliphatic group, or an aryl group.

[0100] From the point of the effects of the present invention, the compounds represented by formula (TS-III) are more preferably those compounds represented by any one of formulae (TS-IIIB), (TS-IIIC), and (TS-IIID), and most preferably those compounds represented by formula (TS-IIIB), or (TS-IIIC).

[0101] The compound represented by formula (TS-IV) is described in more detail below.

[0102] In formula (TS-IV), R_{71} and R_{72} each independently represent an aliphatic group (e.g., methyl, methoxycarbonylethyl, dodecyloxycarbonyl ethyl, benzyl), an aryl group (e.g., phenyl, 4-octyloxyphenyl, 2-butoxy-5-(t)octylphenyl), or a heterocyclic group (e.g., 2-pyridyl, 2-pyrimidyl). Further, R_{71} represents a hydrogen atom, Li, Na, or K. R_{71} and R_{72} may combine together to form a 5- to 7-membered ring, such as a tetrahydrothiophene ring and a thiomorpholine ring. q represents 0, 1, or 2. In the above, the total number of carbon atoms of R_{71} and R_{72} is 10 or more.

[0103] The compound represented by formula (TS-IV) for use in the present invention include those compounds represented by, for example, formula (I) of JP-B-2-44052, formula (T) of JP-A-3-48242, formula (A) of JP-A-3-266836, formula (I), (II) or (III) of JP-A-5-323545, formula (I) of JP-A-6-148837, formula (I) of U.S. Patent No. 4,933,271, and formula (I) of U.S. Patent No. 4,770,987. These compounds can be synthesized according to the method described in these publications or general methods described in Shin Jikken Kagaku Koza, Vol. 14 (Maruzen Co., Ltd.) (1977, 1978).

[0104] From the point of the effects of the present invention, in formula (TS-IV), q is preferably 0 or 2. When q is 0, it is preferable that R_{71} and R_{72} each independently represent an aliphatic group, or an aryl group, or that R_{71} and R_{72} combine together to form a 6-membered ring. When q is 2, it is preferable that R_{71} represents a hydrogen atom, Na, K, an aliphatic group, or an aryl group, and R_{72} represents an aliphatic group, or an aryl group; it is more preferable that R_{71} represents a hydrogen atom, Na, or K, and R_{72} represents an aryl group.

[0105] The compound represented by formula (TS-V) is described in more detail below.

[0106] In formula (TS-V), R_{81}, R_{82}, and R_{83} each independently represent an aliphatic group (e.g., methyl, ethyl, t-octyl, allyl), an aryl group (e.g., phenyl, 4-t-butylphenyl, 4-vinylphenyl), an aliphatic oxy group (e.g., methoxy, t-octyloxy), an aryloxy group (e.g., phenoxy, 2,4-di-t-butylphenoxy), an aliphatic amino group (e.g., butyl amino, dibutyl amino), or an arylamino group (e.g., anilino, 4-methoxyanilino, N-methylanilino), and t represents 0 or 1. Each combination of R_{81} and R_{82}, and R_{81} and R_{83} may combine together to form a 5- to 8-membered ring. Provided that the number of total carbon atoms of R_{81}, R_{82}, and R_{83} is 10 or more (preferably 10 to 50).

[0107] The compound represented by formula (TS-V) for use in the present invention include those compounds represented by, for example, formula (I) of JP-A-3-25437, formula (I) of JP-A-3-142444, formula of U.S. Patent No. 4,749,645, and formula of U.S. Patent No. 4,980,275. These compounds can be synthesized according to the method described in these publications or general methods described in Shin Jikken Kagaku Koza, Vol. 14 (Maruzen Co., Ltd.) (1977, 1978).

[0108] As the compound represented by formula (TS-V), preferred are compounds in which t is 0, and compounds in which t is 1 and at least one of R_{81}, R_{82} and R_{83} is an aliphatic group, an aryl group, an aliphatic amino group, or an arylamino group.

[0109] In formula (TS-V), from the point of the effects of the present invention, preferable is the case where t is 1 and R_{81}, R_{82} and R_{83} each independently represent an aliphatic group, an aryl group, an aliphatic oxy group, an aryloxy, or an arylamino group (more preferably at least one of R_{81}, R_{82}, and R_{83} is an aliphatic group, an aryl group, or an arylamino group). Also preferable is the case where R_{81} and R_{82} combine together to form an 8-membered ring. More preferable is the case where t is 1, and R_{81}, R_{82}, and R_{83} each independently represent an aryl group, an aryloxy group or an arylamino group (more preferably at least one of R_{81}, R_{82}, and R_{83} is an aryl group, or an arylamino group).

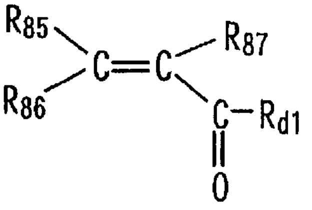
[0110] The compound represented by formula (TS-VI) is described in more detail below.

[0111] In formula (TS-VI), R_{85}, R_{86}, R_{87}, and R_{88} each independently represent a hydrogen atom or a substituent (e.g., an aliphatic group, an aryl group, an aliphatic oxycarbonyl group, an aryl oxycarbonyl group, a phosphoryl group, an acyl amino group, or a carbamoyl group). However, all of R_{85}, R_{86}, R_{87}, and R_{88} simultaneously are not a hydrogen atom. Any two of R_{85}, R_{86}, R_{87}, and R_{88} may combine together to form a 5- to 7-membered ring (e.g., a cyclohexene ring, a cyclohexane ring), however the ring is not an aromatic ring consisting only of carbon atoms. The total number of carbon atoms of the compound represented by formula (TS-VI) is 10 or more (preferably 10 to 50).

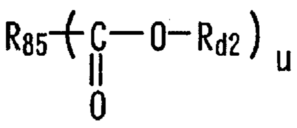
[0112] The compound represented by formula (TS-VI) for use in the present invention include those compounds represented by, for example, formula (I) of U.S. Patent No. 4,713,317, formula (I) of JP-A-8-44017, formula (I) of JP-A-8-44018, formula (I) of JP-A-8-44019, formula (I) or (II) of JP-A-8-44020, formula (I) of JP-A-8-44021 and formula (I) or (II) of JP-A-8-44022. These compounds can be synthesized according to the method described in these publications or general methods described in Shin Jikken Kagaku Koza, Vol. 14 (Maruzen Co., Ltd.) (1977, 1978).

[0113] From the point of the effects of the present invention, the compounds represented by formula (TS-VI) are preferably those compounds represented by any one of formulae (TS-VIA), (TS-VIB), and (TS-VIC).

formula (TS-VIA)

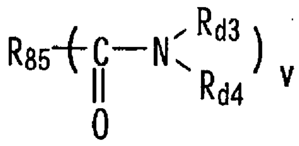


formula (TS-VIB)



$$R_{85}\left(\underset{\underset{O}{\|}}{C}-O-R_{d2}\right)_u$$

formula (TS-VIC)



$$R_{85}\left(\underset{\underset{O}{\|}}{C}-N\begin{matrix}R_{d3}\\R_{d4}\end{matrix}\right)_v$$

[0114] In formulae (TS-VIA), (TS-VIB) and (TS-VIC), R_{85}, R_{86}, and R_{87} each have the same meanings as defined in formula (TS-VI). R_{d1} represents an aliphatic group (e.g., methyl, butyl, t-butyl, dodecyl), an aliphatic oxy group (e.g., methoxy, butoxy, t-butoxy, dodecyloxy, allyloxy), an aryloxy group (e.g., phenoxy, 2,4,6-trimethylphenoxy), an aliphatic amino group (e.g., methyl amino, allyl amino, diallylamino), or an arylamino group (e.g., anilino, N-methylanilino). R_{d2} and R_{d3} each independently represent an alkenyl group (e.g., vinyl, allyl, oleyl). R_{d4} represents a hydrogen atom, an aliphatic group (e.g., methyl, allyl, vinyl, octyl), or an aryl group (e.g., phenyl, naphthyl, 4-vinylphenyl). u and v each independently represent 1, 2 or 3.

[0115] As to the compounds represented by any one of formulae (TS-VIA) to (TS-VIC), substituents preferable from the point of the effects of the present invention are described below.

[0116] In formula (TS-VIA), preferable is the case where R_{85}, R_{86}, and R_{87} each independently represent a hydrogen atom, or an aliphatic group, and R_{d1} is an aliphatic oxy group, an aliphatic amino group, or an arylamino group; and more preferable is the case where R_{85}, R_{86}, and R_{87} each independently represent a hydrogen atom, or an aliphatic group, and R_{d1} is an aliphatic oxy group, or an aliphatic amino group. In formula (TS-VIB), preferable is the case where R_{85} is an aliphatic group or an aryl group, R_{d2} is an alkenyl group, and u is 1, 2 or 3; and more preferable is the case where R_{85} is an aliphatic group or an aryl group, R_{d2} is an alkenyl group, and u is 2 or 3. In formula (TS-VIC), preferable is the case where R_{85} is an aliphatic group or an aryl group, R_{d3} is an alkenyl group, R_{d4} is a hydrogen atom, or an aliphatic group, and u is 1, 2 or 3; and more preferable is the case where R_{85} is an aliphatic group or an aryl group, R_{d3} is an alkenyl group, R_{d4} is a hydrogen atom, or an alkenyl group, and u is 2 or 3.

[0117] From the point of the effects of the present invention, the compounds represented by formula (TS-VI) are preferably those compounds represented by formula (TS-VIA) or (TS-VIB), and most preferably those compounds represented by formula (TS-VIA).

[0118] The metal complex for use in the present invention is explained below.

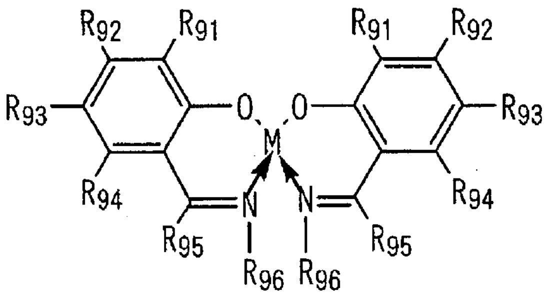
[0119] The metal complex for use in the present invention, is preferably those having Cu, Co, Ni, Pd, or Pt as a central metal, and more preferably those having Ni as a central metal. It is preferable that they are low in solubility to water. Specifically, the solubility at room temperature is preferably 50% or less, more preferably 25% or less, and furthermore preferably 10% or less. The category of a preferable compound can also be defined in terms of total number of carbon atoms of the whole compound. Specifically, the compound has carbon atoms preferably in the range of 15 to 65, more preferably in the range of 20 to 60, furthermore preferably in the range of 25 to 55, and most preferably in the range of 30 to 50, in total.

[0120] The metal complex for use in the present invention may have any kind of ligand. Dithiolate-series metal complexes and salicylaldoxime-series metal complexes are preferable, and salicylaldoxime-series metal complexes are more preferable.

[0121] As the metal complex for use in the present invention, preferred are not only dithiolate-seires nickel complexes and salicylaldoxime-series nickel complexes, but also those described, for example, in, formula (I) of JP-B-61-13736, formula (I) of JP-B-61-13737, formula (I) of JP-B-61-13738, formula (I) of JP-B-61-13739, formula (I) of JP-B-61-13740, formula (I) of JP-B-61-13742, formula (I) of JP-B-61-13743, formula (I) of JP-B-61-13744, formula of JP-B-5-69212, formula (I) or (II) of JP-B-5-88809, formula of JP-A-63-199248, formula (I) or (II) of JP-A-64-75568, formula (I) or (II) of JP-A-3-182749, formula (II), (III), (IV) or (V) of U.S. Patent No. 4,590,153, and formula (II), (III), or (IV) of U.S. Patent No. 4,912,027.

[0122] As the metal complex, the compound represented by formula (TS-VIIA) is preferable from the point of the effects of the present invention.

formula (TS-VIIA)



[0123] In formula (TS-VIIA), R_{91}, R_{92}, R_{93}, and R_{94} each independently represent a hydrogen atom or a substituent (e.g., an aliphatic group, an aliphatic oxy group, an aliphatic sulfonyl group, an aryl sulfonyl group, an acyl amino group). R_{95} represents a hydrogen atom, an aliphatic group (e.g., methyl, ethyl, vinyl, undecyl), or an aryl group (e.g., phenyl, naphthyl). R_{96} represents a hydrogen atom, an aliphatic group (e.g., methyl, ethyl), an aryl group (e.g., phenyl, 4-methylphenyl), or a hydroxyl group. M represents Cu, Co, Ni, Pd, or Pt. Two R_{96}s may combine together to form a 5- to 7-membered ring. R_{91} and R_{92}, R_{92} and R_{93}, R_{93} and R_{94}, and R_{94} and R_{95}, each of which is adjacent to each other, may combine together to form a 5-to 6-membered ring.

[0124] In formula (TS-VIIA), it is preferable from the point of the effects of the present invention that R_{91}, R_{92}, R_{93}, and R_{94} each independently represent a hydrogen atom, an aliphatic group, or an aliphatic oxy group, R_{95} is a hydrogen atom, R_{96} is a hydrogen atom, an aliphatic group, or a hydroxyl group, and M is Ni; and it is more preferable that R_{91}, R_{92}, R_{93}, and R_{94} each independently represent a hydrogen atom, or an aliphatic oxy group, R_{95} is a hydrogen atom, R_{96} is a hydroxyl group, and M is Ni.

[0125] From the point of the effects of the present invention, among the compound represented by any one of formulae (TS-I) to (TS-VI) and the metal complex, preferred are those compounds represented by any one of formulae (TS-I), (TS-II), (TS-IV), (TS-V), and (TS-VI), and most preferred are those compounds represented by any one of formulae (TS-I), (TS-II), (TS-V), and (TS-VI).

[0126] One or more kinds of compounds represented by one of formulae (TS-I) to (TS-VI) or one or more kinds from the metal complexes, for use in the present invention, may be used. Further, those belonging to the different categories (expressed by different formulae or being metal complex) may be used in combination. The above compound(s) and the dye-forming coupler represented by formula (I) or (II) may be added to different layers or to the same layer, and these are preferably added to the same layer. The addition amount of the compound represented by any one of formulae (TS-I) to (TS-VI) and the metal complex, is preferably in the range of 1 to 400 mass%, more preferably in the range of 10 to 300 mass%, most preferably in the range of 25 to 200 mass%, based on the dye-forming coupler represented by formula (I) or (II) respectively.

[0127] In view of effects of the present invention, preferable is the case where at least one compound represented by formula (TS-IB) is used in combination with at least one compound selected from the compounds represented by formula (TS-IE), (TS-IF), or (TS-IG). More preferable is the case where at least one compound represented by formula (TS-IB) is used in combination with at least one compound selected from the compounds represented by formula (TS-IE) or (TS-IG). Further more preferable is the case where at least one compound represented by formula (TS-IB) is used in combination with at least one compound selected from the compounds represented by formula (TS-IE)). These cases are preferable since the effects aimed in the present invention can be attained remarkably.

[0128] Specific examples of the compound represented by any one of formulae (TS-I) to (TS-VI) and the metal complex are shown below. However, the present invention is not limited to these compounds.

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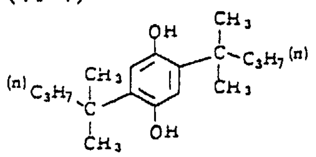

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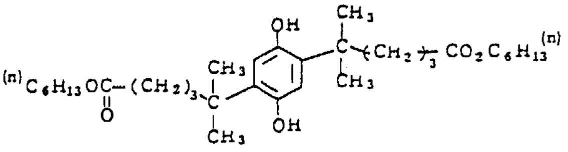

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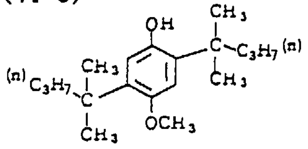

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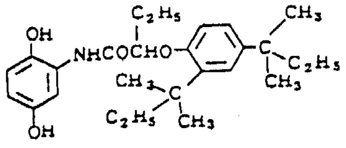

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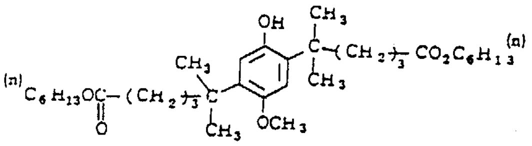

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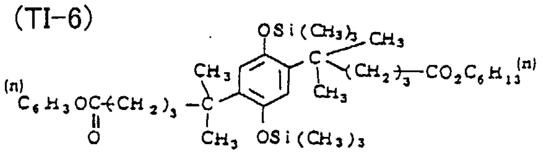

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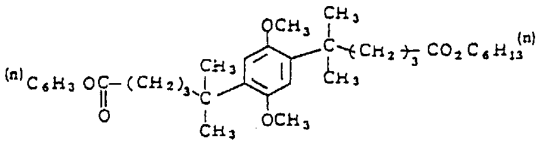

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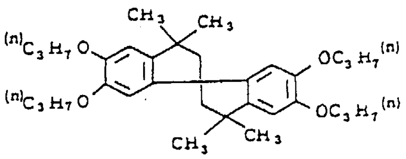

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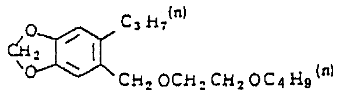

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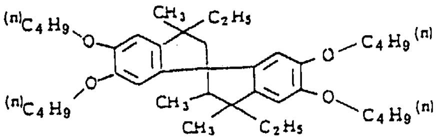

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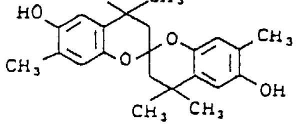

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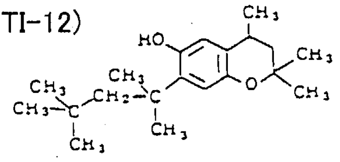

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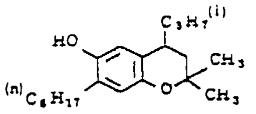

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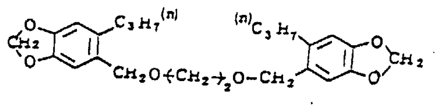

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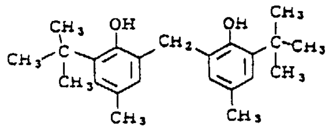

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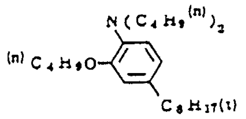

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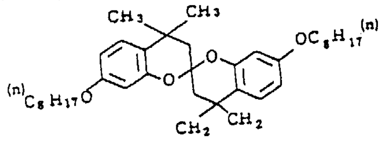

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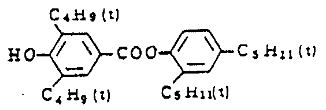

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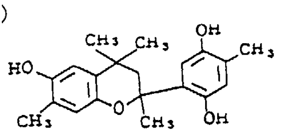

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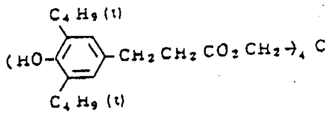

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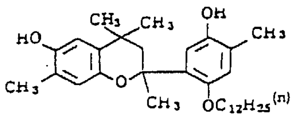

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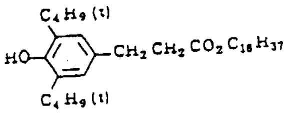

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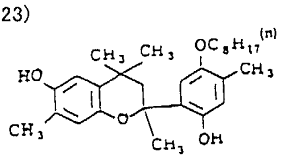

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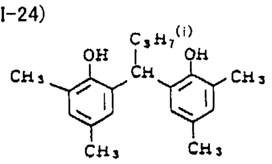

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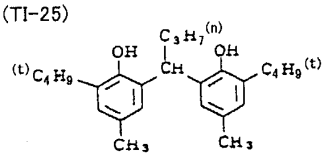

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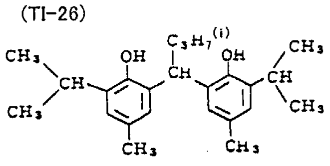

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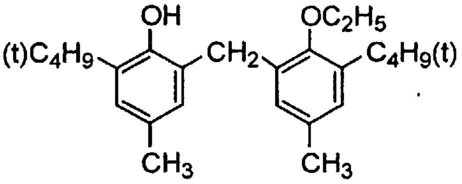

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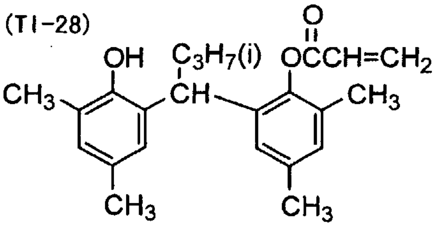

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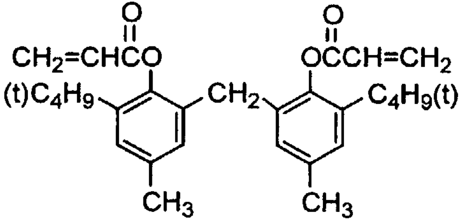

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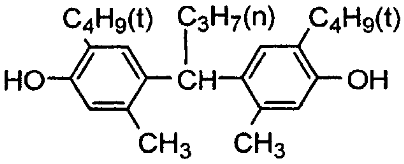

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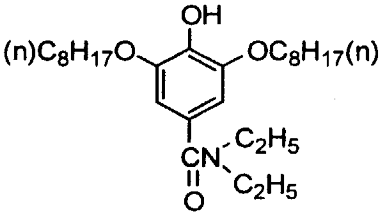

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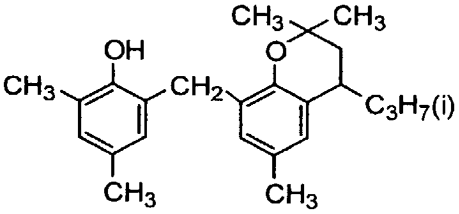

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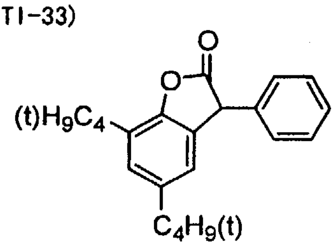

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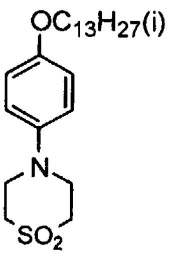

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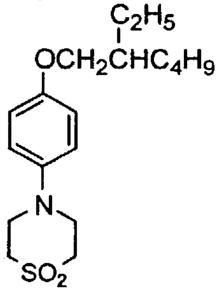

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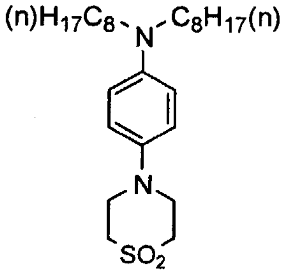

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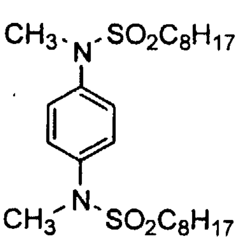

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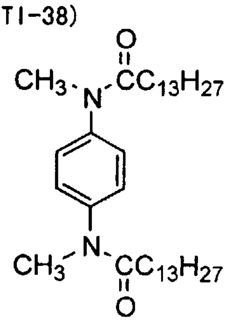

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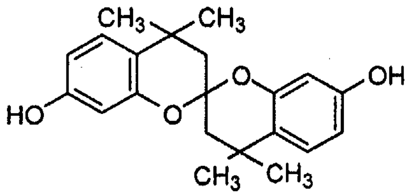

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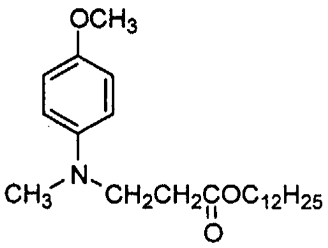

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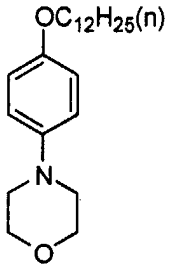

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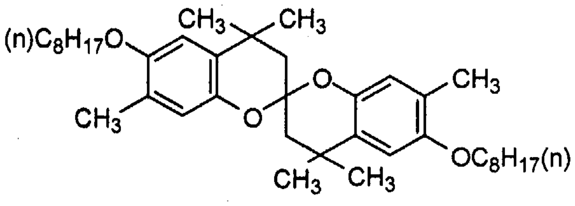

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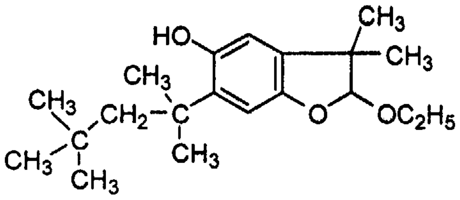

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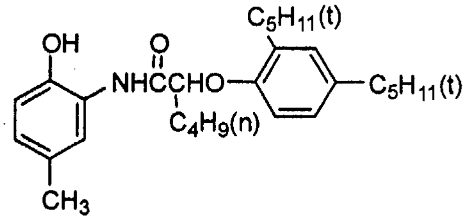

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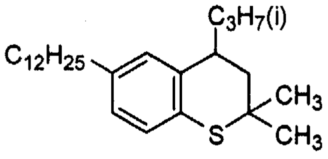

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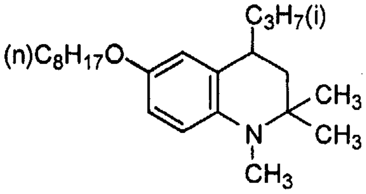

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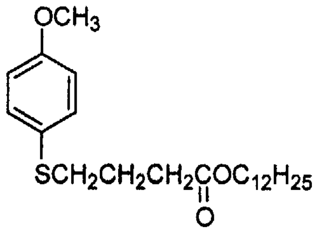

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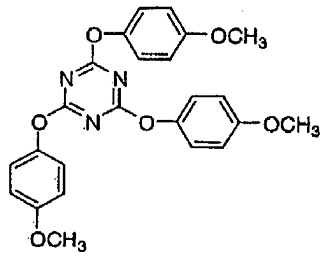

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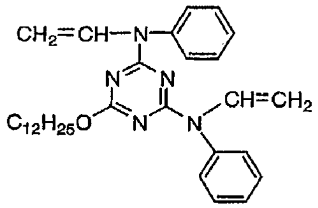

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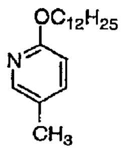

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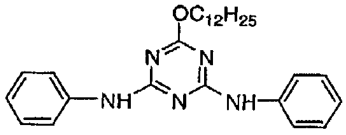

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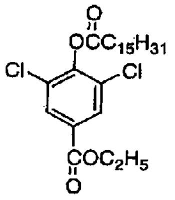

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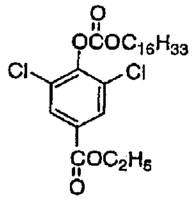

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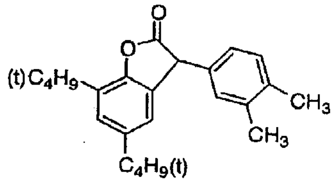

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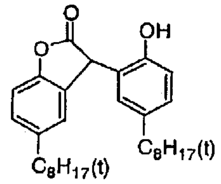

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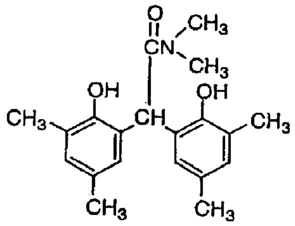

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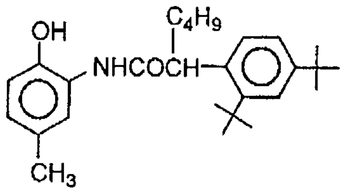

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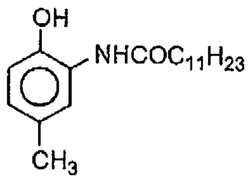

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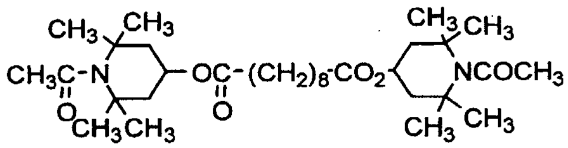

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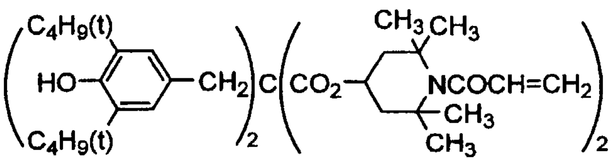

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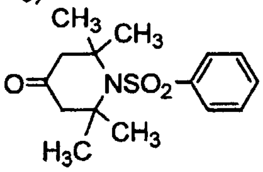

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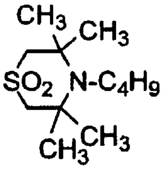

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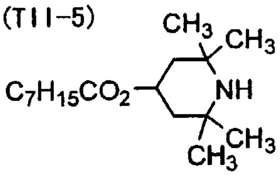

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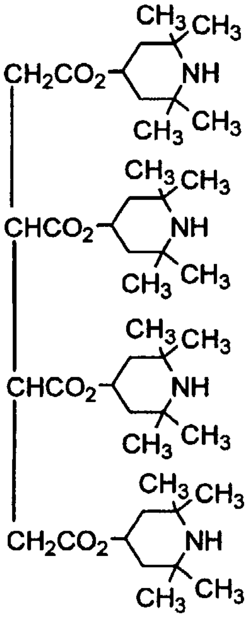
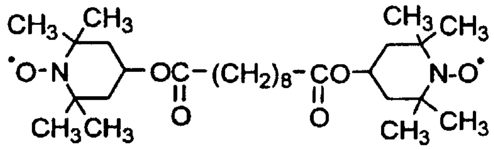
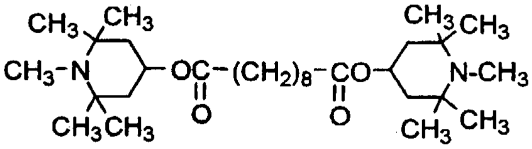


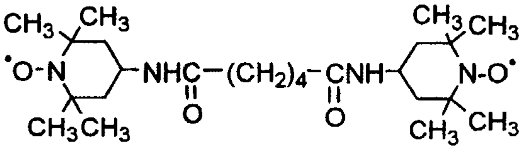
(TII-6)



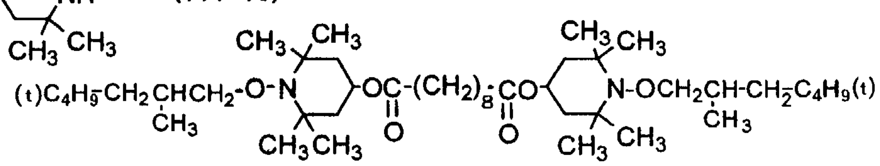
(TII-8)



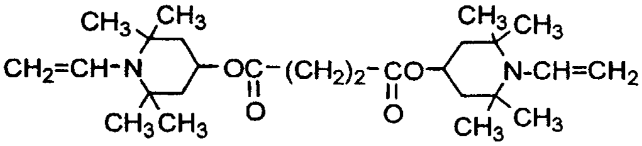
(TII-9)



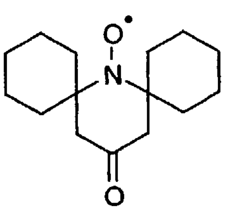
(TII-10)



(TII-11)



(TII-12)



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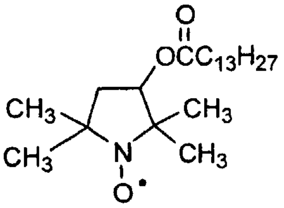

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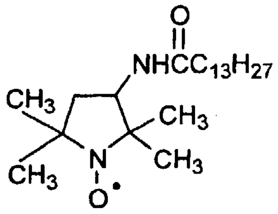
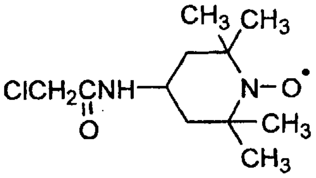
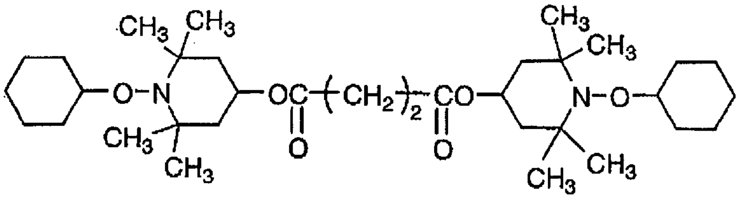


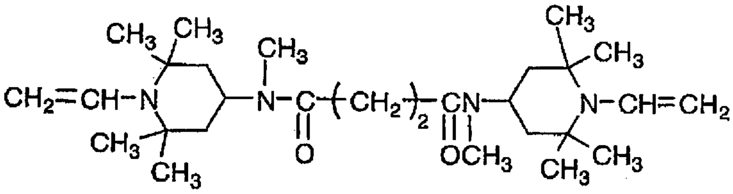
(TII-15)



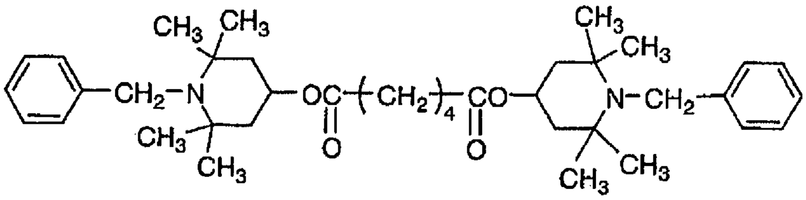
(TII-16)



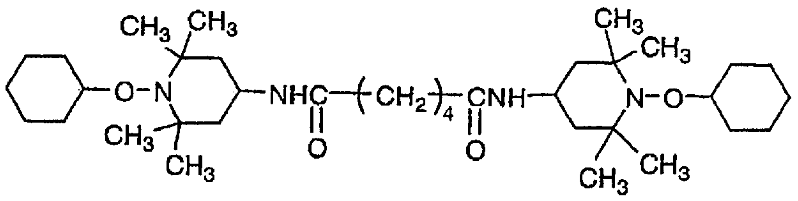
(TII-17)



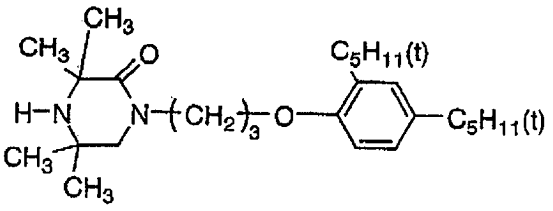
(TII-18)



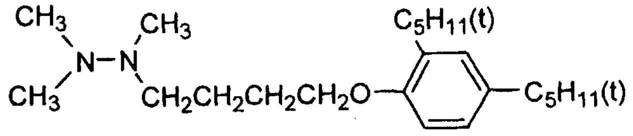
(TII-19)



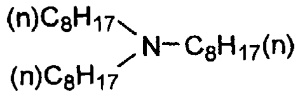
(TII-20)



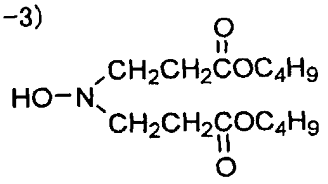
(TIII-1)



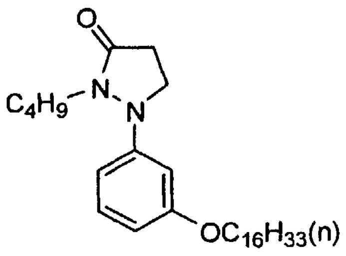
(TIII-2)



(TIII-3)



(TIII-4)



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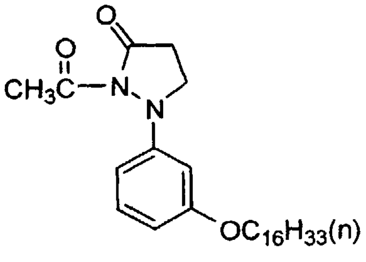

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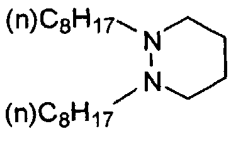
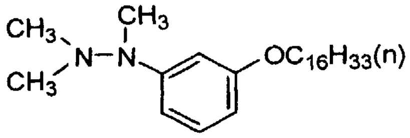
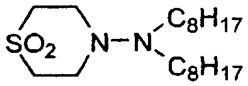


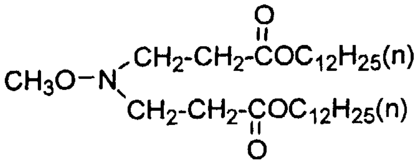
(TIII-7)



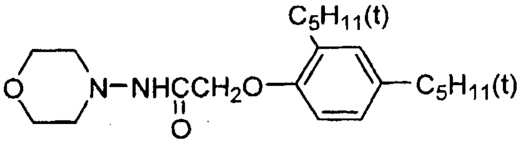
(TIII-8)



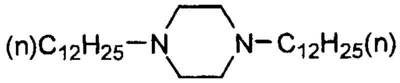
(TIII-9)



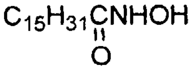
(TIII-10)



(TIII-11)

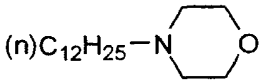


(TIII-12)

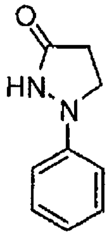


$C_{15}H_{31}\underset{\underset{O}{\|}}{C}NHOH$

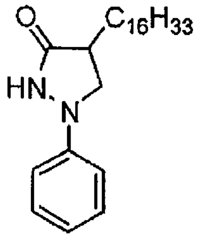
(TIII-13)



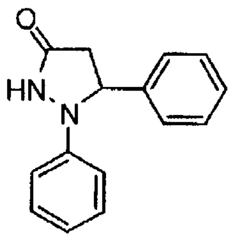
(TIII-14)



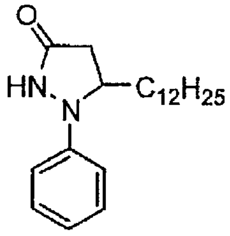
(TIII-15)



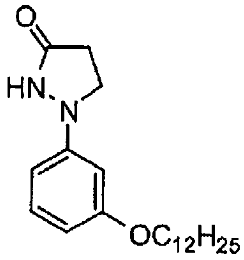
(TIII-16)



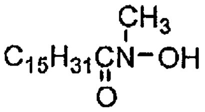
(TIII-17)



(TIII-18)

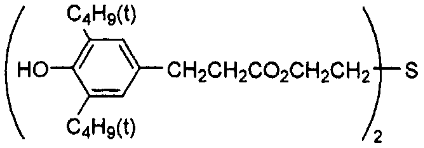


(TIII-19)

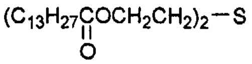


$C_{15}H_{31}\underset{O}{\underset{\|}{C}}\overset{CH_3}{\overset{|}{N}}-OH$

(TIV-1)

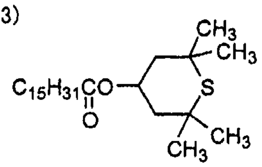


(TIV-2)

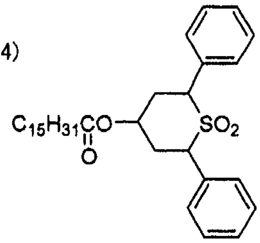


$(C_{13}H_{27}\underset{O}{\underset{\|}{C}}OCH_2CH_2)_2-S$

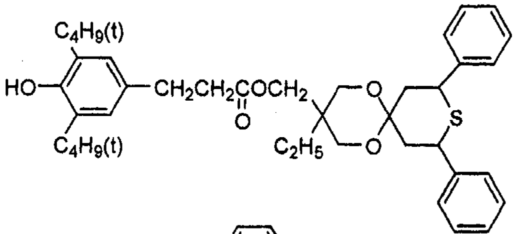
(TIV-3)



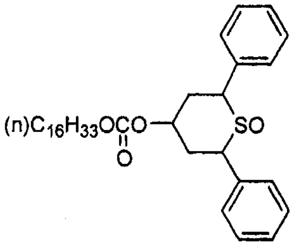
(TIV-4)



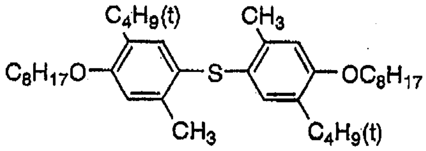
(TIV-5)



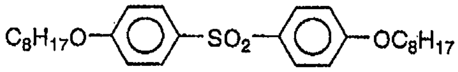
(TIV-6)



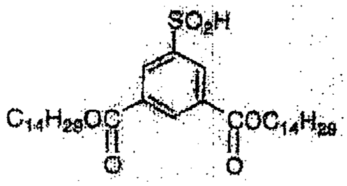
(TIV-7)



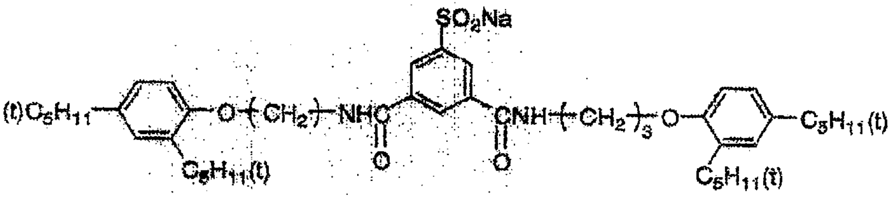
(TIV-8)



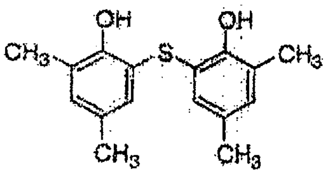
(TIV-9)



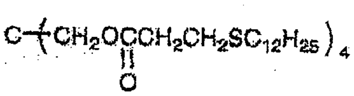
(TIV-10)



(TIV-11)

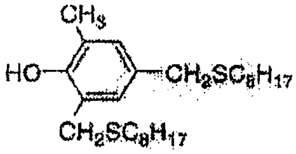


(TIV-12)

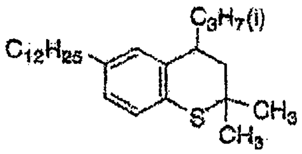


$C\left(CH_2O\underset{\underset{O}{\|}}{C}CH_2CH_2SC_{12}H_{25}\right)_4$

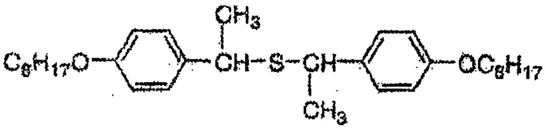
(TIV-13)



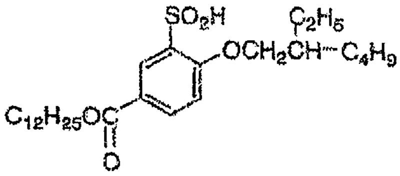
(TIV-14)



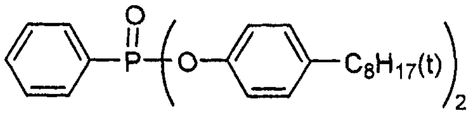
(TIV-15)



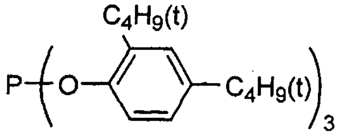
(TIV-16)



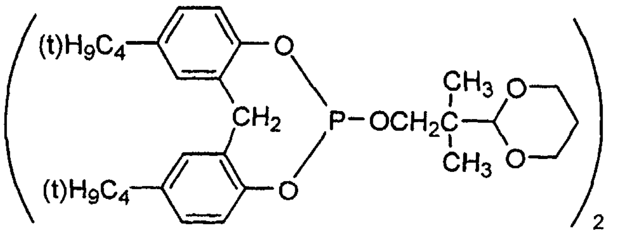
(TV-1)



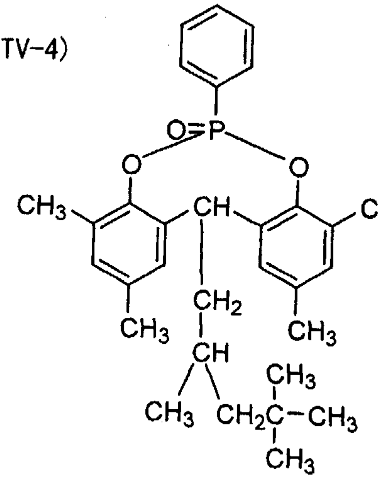
(TV-2)



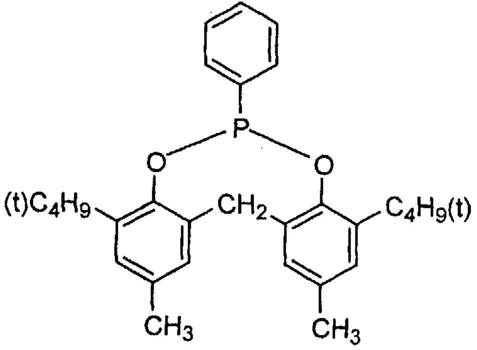
(TV-3)



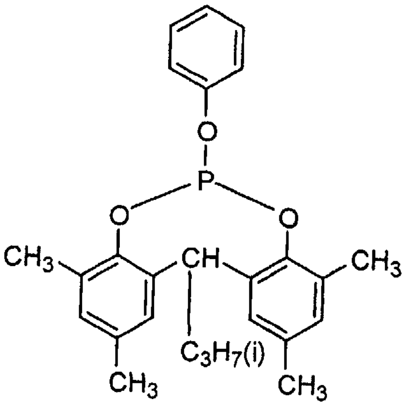
(TV-4)



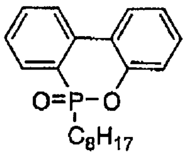
(TV-5)



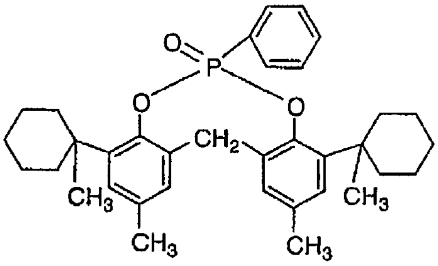
(TV-6)



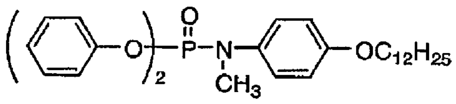
(TV-7)



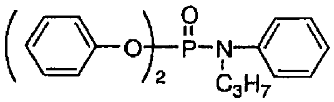
(TV-8)



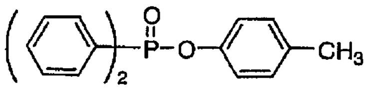
(TV-9)



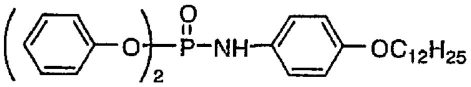
(TV-10)



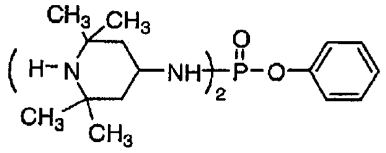
(TV-11)



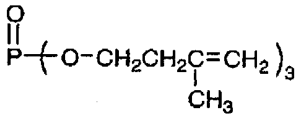
(TV-12)



(TV-13)

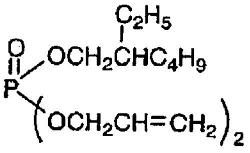


(TV-14)



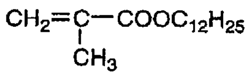
$O=P\left(-O-CH_2CH_2C(CH_3)=CH_2\right)_3$

(TV-15)



$O=P(OCH_2CH(C_2H_5)C_4H_9)(OCH_2CH=CH_2)_2$

(TVI-1)



$CH_2=C(CH_3)-COOC_{12}H_{25}$

(TVI-2)

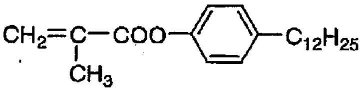
$CH_2=CH-COOC_{12}H_{25}$

(TVI-3) $CH_3CH=CH-COOC_{12}H_{25}$

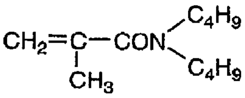
(TVI-4)

$CH_2=CH-COOCH_2CH=CH(CH_2)_3CH=CH_2$

(TVI-5)

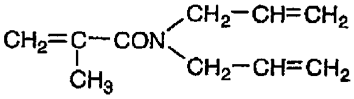


(TVI-6)



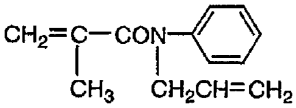
$CH_2=C(CH_3)-CON(C_4H_9)_2$

(TVI-7)

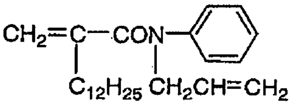


$CH_2=C(CH_3)-CON(CH_2-CH=CH_2)_2$

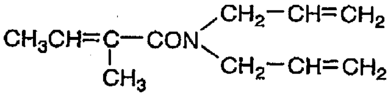
(TVI-8)



(TVI-9)

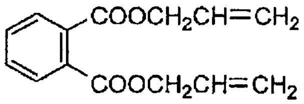


(TVI-10)

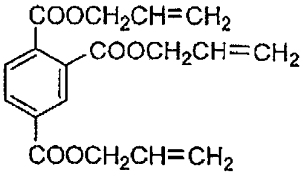


$CH_3CH=C(CH_3)-CON(CH_2-CH=CH_2)_2$

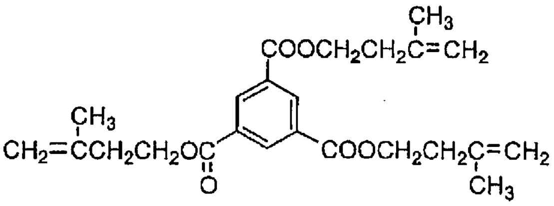
(TVI-11)



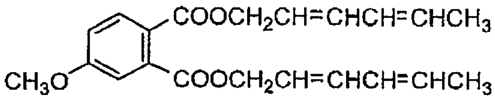
(TVI-12)



(TVI-13)



(TVI-14)



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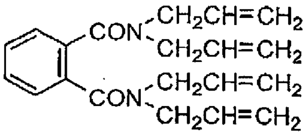

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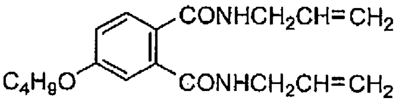

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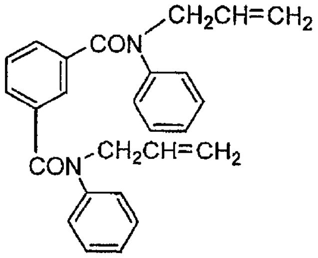

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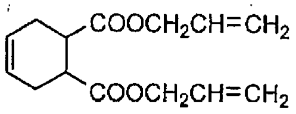

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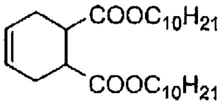
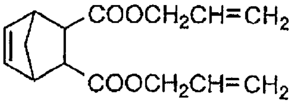
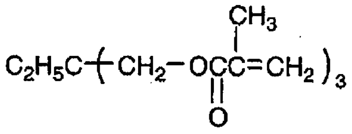


(TVI-20)

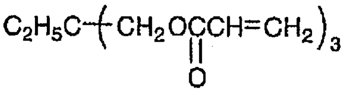


(TVI-21)



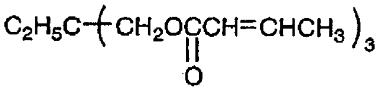
$C_2H_5C\left(CH_2-O\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}=CH_2\right)_3$

(TVI-22)



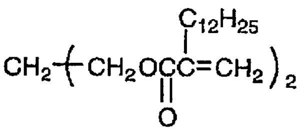
$C_2H_5C\left(CH_2O\underset{\underset{O}{\|}}{C}CH=CH_2\right)_3$

(TVI-23)



$C_2H_5C\left(CH_2O\underset{\underset{O}{\|}}{C}CH=CHCH_3\right)_3$

(TVI-24)

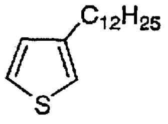


$CH_2\left(CH_2O\underset{\underset{O}{\|}}{C}\overset{\overset{C_{12}H_{25}}{|}}{C}=CH_2\right)_2$

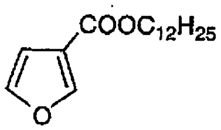
(TVI-25)

$CH_2=CHCH_2SCH_2COOC_{12}H_{25}$

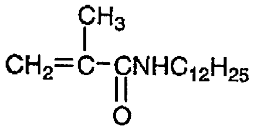
(TVI-26)



(TVI-27)

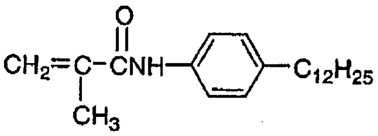


(TVI-28)

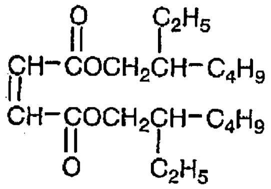


$CH_2=C(CH_3)-C(=O)NHC_{12}H_{25}$

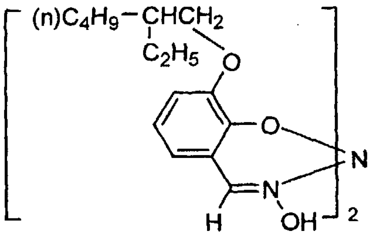
(TVI-29)



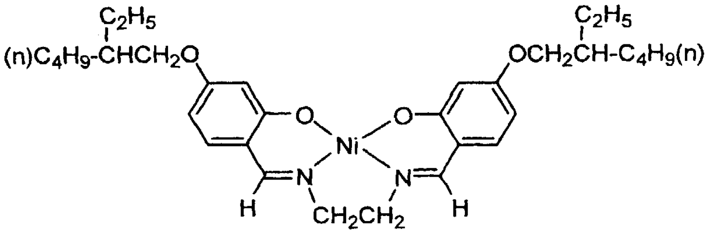
(TVI-30)



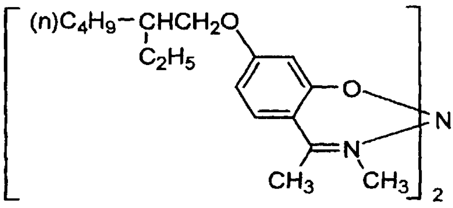
(TVII-1)



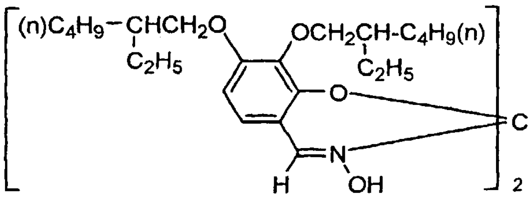
(TVII-2)



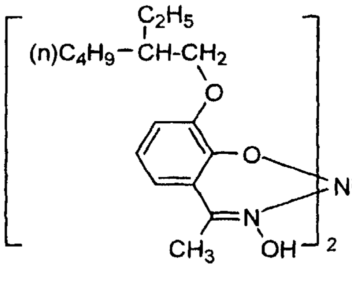
(TVII-3)



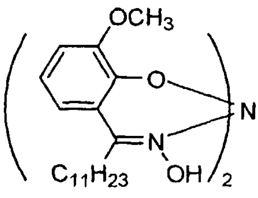
(TVII-4)



(TVII-5)



(TVII-6)



[0129] In combination with the compound represented by any one of formulae (TS-I) to (TS-VI) for use in the present invention, other compounds may be used additionally. Examples of the compounds that may be used in combination include boron compounds represented by formula (I) in JP-A-4-174430, epoxy compounds represented by formula (II) in U.S. Patent No. 5,183,731 and formula (S1) in JP-A-8-53431, disulfide-series compounds represented by formula in European Patent Publication EP271,322 B1 and formula (I), (II), (III) or (IV) in JP-A-4-19736, reactive compounds represented by formula (I), (II), (III) or (IV) in U.S. Patent No. 5,242,785, cyclic phosphorous compounds represented by formula (1) in JP-A-8-283279, alcoholic compounds represented by formula (SO) in JP-A-7-84350, formula (G) in JP-A-9-114061, formula (II) in JP-A-9-146242, formula (A) in JP-A-9-329876, and formula (VII) in JP-A-62-175748. If the above-mentioned publications include exemplified compounds that are embraced in formulae (TS-I) to (TS-VI) for use in the present invention, these compounds are also included in the examples of the compounds for use in the present invention.

[0130] It is sufficient that the light-sensitive material of the present invention has, on a support, at least one layer containing a yellow dye-forming coupler for use in the present invention. The coupler is incorporated in a hydrophilic colloid layer composed of a general gelatin binder. A general light-sensitive material can be formed by providing, on a support, at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer, and at least one red-sensitive silver halide emulsion layer. The order of these layers are not particularly limited. Further, an infrared-sensitive silver halide emulsion layer may be used in place of one of the above-mentioned light-sensitive emulsion layers. Color reproduction based on subtractive color processes can be performed by incorporating, into each of these light-sensitive emulsion layers, a silver halide emulsion having sensitivity in the corresponding wavelength range, and a coupler for forming a dye having a color complementary to the color of sensitizing light. However, the light-sensitive material may have such a construction that the light-sensitive emulsion and the developed hue of the coupler do not have the above-mentioned corresponding relation.

[0131] The coupler for use in the present invention is useful as a yellow coupler in a conventional color photographic light-sensitive material that uses p-phenylenediamine compounds as a color-developing agent. The coupler may be incorporated in any one of the light-sensitive silver halide emulsion layers. Further, the coupler is also useful as a dye-forming coupler that gives a dye having a hue of various types, in systems in which color-developing agents other than p-phenylenediamine compounds are used.

[0132] The yellow dye-forming coupler represented by formula (I) or (II), the compound represented by any one of formulae (TS-I) to (TS-VI), the metal complex, and the like additives for use in the present invention may be introduced into the light-sensitive material according to known dispersion methods. It is preferable to use a water-in-oil dispersion method in which such a compound is dissolved in a high-boiling organic solvent (optionally in combination with a low-boiling organic solvent), and the solution is emulsified and dispersed in an aqueous gelatin solution, and then it is added to a silver halide emulsion. Further, it is preferable to use the metal complex for use in the present invention with dispersing it with a high-boiling organic solvent.

[0133] Examples of the high-boiling organic solvent that can be used in a water-in-oil dispersion method are described, for example, in U.S. Patent No. 2,322,027. Further, specific examples of a latex dispersion method as one of polymer dispersion methods are described, for example, in U.S. Patent No. 4,199,363, West German Patent (OLS) No. 2,541,274, JP-B-53-41091, European Patent Publication EP0,727,703 A1, and EP0,727,704 A1. Further, a dispersion method using a polymer that is soluble in an organic solvent is described in PCT International Publication WO88/723.

[0134] Examples of the high-boiling organic solvent that can be used in a water-in-oil dispersion method include phthalic acid esters (e.g., dibutyl phthalate, dioctyl phthalate, di-2-ethylhexyl phthalate), esters of phosphoric acid or phosphonic acid (e.g., triphenyl phosphate, tricresyl phosphate, tri-2-ethylhexyl phosphate), fatty acid esters (e.g., di-2-ethylhexyl succinate, tributyl citrate), benzoic acid esters (e.g., 2-ethylhexyl benzoate, dodecyl benzoate), amides (e.g., N,N-diethyldodecane amide, N,N-dimethylolein amide), alcohols or phenols (e.g., iso-stearyl alcohol, 2,4-di-tert-amyl phenol), anilines (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), chlorinated paraffins, hydrocarbons (e.g., dodecyl benzene, diisopropyl naphthalene), and carboxylic acids (e.g., 2-(2,4-di-tert-amyl phenoxy)butyrate). Further, the high-boiling point organic solvent may be used in combination with an auxiliary solvent having a boiling point of 30 °C or more and 160 °C or less, such as ethyl acetate, butyl acetate, methyl ethyl ketone, cyclohexanone, methylcellosolve acetate, and dimethylformamide. The high-boiling organic solvent is preferably used in an amount of 0 to 10 times (more preferably 0 to 4 times) that of a coupler, in terms of mass ratio.

[0135] All or a part of the auxiliary solvent may be removed from an emulsified dispersion by means of a vacuum distillation, a noodle washing, an ultrafiltration, or the like, as occasion demands, for the purpose of improving storage stability with the lapse of time in the state of the emulsified dispersion, or inhibiting a fluctuation in photographic properties or improving stability with the lapse of time of the final coating composition in which the emulsified dispersion is mixed with a silver halide emulsion.

[0136] The average particle size of the oleophilic fine particle dispersion thus obtained is preferably in the range of 0.04 to 0.50 μm, more preferably in the range of 0.05 to 0.30 μm, and most preferably in the range of 0.08 to 0.20 μm. The average particle size can be determined with a measuring device such as Coulter submicron particle analyzer model N4 (trade name, manufactured by Coulter Electronics Co., Ltd.).

[0137] Other known photographic materials and additives may be used in the silver halide photographic light-sensitive material of the present invention.

[0138] For example, as a photographic support (base), a transmissive type support and a reflective type support may be used. As the transmissive type support, it is preferred to use a transparent support, such as a cellulose nitrate film, and a transparent film of polyethylene terephthalate, or a polyester of 2,6-naphthalenedicarboxylic acid (NDCA) and ethylene glycol (EG), or a polyester of NDCA, terephthalic acid, and EG, provided thereon with an information-recording layer such as a magnetic layer. As the reflective type support, it is especially preferable to use a reflective support having a substrate laminated thereon with a plurality of polyethylene layers or polyester layers (water-proof resin layers or laminate layers), at least one of which contains a white pigment such as titanium oxide.

[0139] It is preferred for the above-mentioned waterproof resin layer to contain a fluorescent brightening agent. A fluorescent brightening agent may be dispersed in a hydrophilic colloid layer of the light-sensitive material. As the fluorescent brightening agent, preferred are bezoxazole-series agents, coumarine-series agents and pyrazoline-series agents, and more preferred are bezoxazolyl naphthalene-series agents and bezoxazolyl stilbene-series agents. The amount of the fluorescent brightening agent to be used is not particularly limited, and preferably in the range of 1 to 100 mg/m^2. When the fluorescent brightening agent is mixed with the waterproof resin, a mixing ratio of the fluorescent brightening agent to the waterproof resin is preferably in the range of 0.0005 to 3 mass%, more preferably in the range of 0.001 to 0.5 mass%, based on the resin.

[0140] Further, a transmissive type support or the foregoing reflective type support each having coated thereon a hydrophilic colloid layer containing a white pigment may be used as the reflective type support.

[0141] Furthermore, a reflective type support having a mirror plate reflective metal surface or a secondary diffusion reflective metal surface may be employed as the reflective type support.

[0142] A more preferable reflective support for use in the present invention is a support having a paper substrate provided with a polyolefin layer having fine holes, on the side to which silver halide emulsion layers are to be provided. The polyolefin layer may be composed of multilayers. In this case, it is more preferable for the support to be composed of a fine hole-free polyolefin (e.g., polypropylene, polyethylene) layer adjacent to a gelatin layer on the same side as the silver halide emulsion layers, and a fine hole-containing polyolefin (e.g., polypropylene, polyethylene) layer closer to the paper substrate. The density of the multi-layer or single-layer of polyolefin layer(s) existing between the paper substrate and photographic constituting layers is preferably in the range of 0.40 to 1.0 g/ml, and more preferably in the range of 0.50 to 0.70 g/ml. Further, the thickness of the multi-layer or single-layer of polyolefin layer(s) existing between the paper substrate and photographic constituting layers is preferably in the range of 10 to 100 μm, and more preferably in the range of 15 to 70 μm. Further, the ratio of thickness of the polyolefin layer(s) to the paper substrate is preferably in the range of 0.05 to 0.2, and more preferably in the range 0.1 to 0.5. Further, it is also preferable for enhancing rigidity (mechanical strength) of the reflective support, to provide a polyolefin layer on the side of the foregoing paper substrate opposite to the side of the photographic constituting layers, i.e., on the back surface of the paper substrate.

In this case, it is preferable that the polyolefin layer on the back surface be polyethylene or polypropylene, the surface of which is matted, with the polypropylene being more preferable. The thickness of the polyolefin layer on the back surface is preferably in the range of 5 to 50 μm, and more preferably in the range of 10 to 30 μm, and further the density thereof is preferably in the range of 0.7 to 1.1 g/ml. As to the reflective support for use in the present invention, preferable embodiments of the polyolefin layer to be provided on the paper substrate include those described in JP-A-10-333277, JP-A-10-333278, JP-A-11-52513, JP-A-11-65024, European Patent Nos. 0880065 and 0880066.

[0143] Silver halide grains in the silver halide emulsion which can be used in the present invention, are preferably cubic or tetradecahedral crystal grains substantially having {100} planes (these grains may be rounded at the apexes thereof and further may have planes of higher order), or octahedral crystal grains. Alternatively, a silver halide emulsion in which the proportion of tabular grains having an aspect ratio of 2 or more and composed of {100} or {111} planes accounts for 50% or more in terms of the total projected area, can also be preferably used. The term "aspect ratio" refers to the value obtained by dividing the diameter of the circle having an area equivalent to the projected area of an individual grain by the thickness of the grain. In the present invention, cubic grains, or tabular grains having {100} planes as major faces, or tabular grains having {111} planes as major faces are preferably used.

[0144] As a silver halide emulsion which can be used in the present invention, for example, silver chloride, silver bromide, silver iodobromide, or silver chloro(iodo)bromide emulsions may be used. It is preferable for a rapid processing to use a silver chloride or silver chlorobromide emulsion having a silver chloride content of 95 mol% or greater, and more preferably a silver halide emulsion having a silver chloride content of 98 mol% or greater. Among these silver halide emulsions, those emulsions composed of silver chloride grains each having a silver bromide-localized phase on the surface of a grain are particularly preferable, since both high sensitivity and stabilization of photographic performances are attained.

[0145] The silver bromide-localized phase (silver bromide-rich phase) is preferably formed by epitaxially growing a localized phase having a silver bromide content of at least 10 mole% in terms of the total silver bromide content in the silver bromide-rich phase. The silver bromide content in the silver bromide-rich phase is preferably in the range of 10 to 60 mole%, and most preferably in the range of 20 to 50 mole%. The silver bromide-rich phase is composed of silver in an amount of preferably 0.1 to 5 mole%, more preferably 0.3 to 4 mole%, based on the amount of entire silver constituting the silver halide grains for use in the present invention. A Group VIII metal complex ion, such as $IrCl_6^{3-}$, can be preferably incorporated in the silver bromide-rich phase.

[0146] In the silver halide emulsions for use in the present invention, various kinds of polyvalent metal impurities may be introduced during formation or physical ripening of emulsion grains. Examples of the compounds that can be used include salts or complex salts of group VIII metals in the periodic table, such as iron, iridium, ruthenium, osmium, rhenium, rhodium, cadmium, zinc, lead, copper, and thallium. These compounds may be used in combination. In the present invention, compounds composed of a metal, such as iron, ruthenium, osmium or rhenium, and at least four (4) cyano ligands are especially preferable, from the view points that a high intensity illumination sensitivity is further enhanced, whereas a latent image sensitization is refrained. Further, iridium compounds also provide an outstanding effect on giving suitability to the high illumination intensity exposure. The addition amount of these compounds varies in a wide range according to the purposes for uses, but preferably it is in the range of 10^{-9} to 10^{-2} mole per mole of silver halide.

[0147] The silver halide emulsion for use in the present invention is generally subjected to chemical sensitization. Chemical sensitization can be performed by utilizing a sulfur sensitization represented by the addition of an unstable sulfur compound, a noble metal sensitization represented by gold sensitization, a reduction sensitization, and the like methods, each singly or in combination thereof. Compounds that are preferably used in chemical sensitization include those described in JP-A-62-215272, from page 18, right lower column to page 22, right upper column. Of these chemical sensitization, gold-sensitized silver halide emulsion are particularly preferred, since fluctuation in photographic properties which occurs when scanning exposure with laser beams or the like is conducted, can be further reduced by gold sensitization. In order to conduct gold sensitization, compounds such as chloroauric acid or a salt thereof, gold thiocyanates, gold thiosulfates, and colloidal gold sulfide may be used. The amount of these compounds to be added can vary in a wide range depending on the occasion, and it is generally in the range of 5×10^{-7} mole to 5×10^{-3} mole, and preferably in the range of 1.0×10^{-6} mole to 1×10^{-4} mole, per mole of silver halide. In the present invention, gold sensitization may be used in combination with other sensitizing methods, for example, sulfur sensitization, selenium sensitization, tellurium sensitization, reduction sensitization, or noble metal sensitization using a noble metal compound other than gold compounds.

[0148] The silver halide photographic light-sensitive material of the present invention can be used for various materials such as color negative films, color positive films, color reversal films, color reversal papers, color papers, motion-picture color negatives, motion-picture color positives, display photosensitive materials, and color proof (especially, digital color proof) photosensitive materials.

[0149] The light-sensitive material of the present invention preferably has at least one yellow color-forming silver halide emulsion layer, at least one magenta color-forming silver halide emulsion layer, and at least one cyan color-forming silver halide emulsion layer.

[0150] The yellow coupler-containing silver halide emulsion layer may be disposed at any position on a support. Further, in the case where the silver halide tabular grains are contained in the yellow coupler-containing layer, it is preferable that the yellow coupler-containing layer is positioned more apart from the support than at least one of the magenta coupler-containing silver halide emulsion layer and the cyan coupler-containing silver halide emulsion layer. Further, it is preferable that the yellow coupler-containing silver halide emulsion layer is positioned most apart from the support of other silver halide emulsion layers, from the viewpoints of color-development acceleration, desilvering acceleration, and lowering of a residual color due to a sensitizing dye. Further, it is preferable that the cyan coupler-containing silver halide emulsion layer is positioned in the middle of other silver halide emulsion layers, from the viewpoint of reduction in a blix fading. On the other hand, it is preferable that the cyan coupler-containing silver halide emulsion layer is the lowest layer, from the viewpoint of reduction in a light fading. Further, each of a yellow-color-forming layer, a magenta-color-forming layer and a cyan-color-forming layer may be composed of two or three layers. It is also preferable that a color-forming layer is formed by disposing a silver halide emulsion-free layer containing a coupler, in adjacent to a silver halide emulsion layer, as described in, for example, JP-A-4-75055, JP-A-9-114035, JP-A-10-246940, and US Patent No. 5,576,159.

[0151] With respect to the above-mentioned reflection type support and the silver halide emulsions, and further the kinds of foreign metal ions to be doped in silver halide grains, storage stabilizers and antifoggants for silver halide emulsions, chemical sensitization methods (sensitizers), spectral sensitization methods (spectral sensitizers), cyan, magenta, and yellow couplers and emulsifying and dispersing methods of them, dye-image-preservability improving agents (such as anti-staining agents and discoloration inhibitors), dyes (colored layers), kinds of gelatin, layer structures, film pH of photosensitive materials, and the like, those described in the patent publications shown in the following Table 1 are preferably used.

Table 1

Element	JP-A-7-104448	JP-A-7-77775	JP-A-7-301895
Reflective-type bases	Column 7, line 12 to Column 12, line 19	Column 35, line 43 to Column 44, line 1	Column 5, line 40 to Column 9, line 26
Silver halide emulsions	Column 72, line 29 to Column 74, line 18	Column 44, line 36 to Column 46, line 29	Column 77, line 48 to Column 80, line 28
Different metal ion species	Column 74, lines 19 to 44	Column 46, line 30 to Column 47, line 5	Column 80, line 29 to Column 81, line 6
Storage stabilizers or antifoggants	Column 75, lines 9 to 18	Column 47, lines 20 to 29	Column 18, line 11 to Column 31, line 37 (Especially, mercaptoheterocyclic compounds)
Chemical sensitizing methods (Chemical sensitizers)	Column 74, line 45 to Column 75, line 6	Column 47, lines 7 to 17	Column 81, lines 9 to 17
Spectrally sensitizing methods (Spectral sensitizers)	Column 75, line 19 to Column 76, line 45	Column 47, line 30 to Column 49, line 6	Column 81, line 21 to Column 82, line 48
Cyan couplers	Column 12, line 20 to Column 39, line 49	Column 62, line 50 to Column 63, line 16	Column 88, line 49 to Column 89, line 16
Yellow couplers	Column 87, line 40 to Column 88, line 3	Column 63, lines 17 to 30	Column 89, lines 17 to 30
Magenta couplers	Column 88, lines 4 to 18	Column 63, line 3 to Column 64, line 11	Column 31, line 34 to Column 77, line 44 and column 88, lines 32 to 46
Emulsifying and dispersing methods of couplers	Column 71, line 3 to Column 72, line 11	Column 61, lines 36 to 49	Column 87, lines 35 to 48

Table 1 (Continued)

Element	JP-A-7-104448	JP-A-7-77775	JP-A-7-301895
Dye-image-preservability improving agents (antistaining agents)	Column 39, line 50 to Column 70, line 9	Column 61, line 50 to Column 62, line 49	Column 87, line 49 to Column 88, line 48
Anti-fading agents	Column 70, line 10 to Column 71, line 2		
Dyes (coloring layers)	Column 77, line 42 to Column 78, line 41	Column 7, line 14 to Column 19, line 42, and Column 50, line 3 to Column 51, line 14	Column 9, line 27 to Column 18, line 10
Gelatins	Column 78, lines 42 to 48	Column 51, lines 15 to 20	Column 83, lines 13 to 19
Layer construction of light-sensitive materials	Column 39, lines 11 to 26	Column 44, lines 2 to 35	Column 31, line 38 to Column 32, line 33
Film pH of light-sensitive materials	Column 72, lines 12 to 28		
Scanning exposure	Column 76, line 6 to Column 77, line 41	Column 49, line 7 to Column 50, line 2	Column 82, line 49 to Column 83, line 12
Preservatives in developing solution	Column 88, line 19 to Column 89, line 22		

[0152] As other cyan, magenta, and yellow couplers, which can be used in combination in the present invention, those disclosed in JP-A-62-215272, page 91, right upper column line 4 to page 121, left upper column line 6; JP-A-2-33144, page 3, right upper column line 14 to page 18, left upper column bottom line, and page 30, right upper column line 6 to page 35, right under column, line 11; and European Patent No. 0355,660 (A2), page 4 lines 15 to 27, page 5 line 30 to page 28 bottom line, page 45 lines 29 to 31, page 47 line 23 to page 63 line 50, are also advantageously used.

[0153] Further, it is preferred for the present invention to add compounds represented by formula (II) or (III) in WO 98/33760 or compounds represented by formula (D) described in JP-A-10-221825.

[0154] As fungiproofing/mildewproofing agents that can be used in the present invention, those described in JP-A-63-271247 are useful. As the hydrophilic colloid used for a photographic layer constituting the light-sensitive material, gelatin is preferable, and particularly, those in which heavy metals, such as iron, copper, zinc and manganese, contained as impurities, are preferably 5 ppm or less, and more preferably 3 ppm or less.

[0155] The light-sensitive material of the present invention can preferably be used, in addition to the printing system using a general negative printer, in a scanning exposure system using a cathode ray tube (CRT).

[0156] The cathode ray tube exposure apparatus is simpler and more compact, and therefore less expensive than a laser-emitting apparatus. Further, optical axis and color (hue) can easily be adjusted.

[0157] In a cathode ray tube that is used for image-wise exposure, various light-emitting substances which emit a light in the spectral region, are used as occasion demands. For example, any one of red-light-emitting substances, green-light-emitting substances, blue-light-emitting substances, or a mixture of two or more of these light-emitting substances may be used. The spectral regions are not limited to the above red, green and blue, and fluorescent substances which can emit a light in a region of yellow, orange, purple or infrared can be used. Particularly, a cathode ray tube that emits a white light by means of a mixture of these light-emitting substances is often used.

[0158] When the light-sensitive material has a plurality of light-sensitive layers having different spectral sensitivity distributions and a cathode ray tube has fluorescent substances emitting lights in a plurality of spectral regions, a plurality of colors may be exposed at the same time, i.e., image signals of a plurality of colors may be input to the cathode ray tube and emitted from the tube surface. Alternatively, an exposure method comprising inputting an image signal of each color in order, and emitting light of each color in order through a filter cutting other colors than that color (i.e., area sequential exposure) may be adopted. In general, such an area sequential exposure is preferred for obtaining a high quality image because a cathode ray tube having high resolving power can be used.

[0159] The light-sensitive material of the present invention can preferably be used in the digital scanning exposure system using monochromatic high density light, such as a gas laser, a light-emitting diode, a semiconductor laser, a second harmonic generation light source (SHG) comprising a combination of nonlinear optical crystal with a semiconductor or a solid state laser using a semiconductor laser as an excitation light source. It is preferred to use a semiconductor laser, or a second harmonic generation light source (SHG) comprising a combination of nonlinear optical crystal with a solid state laser or a semiconductor laser, to make a system more compact and inexpensive. In particular, to design a compact and inexpensive apparatus having a longer duration of life and high stability, use of a semiconductor laser is preferable; and it is preferred that at least one of exposure light sources should be a semiconductor laser.

[0160] When such a scanning exposure light source is used, the maximum spectral sensitivity wavelength of the light-sensitive material of the present invention can be arbitrarily set up in accordance with the wavelength of a scanning exposure light source to be used. Since oscillation wavelength of a laser can be made half, using a SHG light source obtainable by a combination of a nonlinear optical crystal with a semiconductor laser or a solid state laser using a semiconductor as an excitation light source, blue light and green light can be obtained. Accordingly, it is possible to have the spectral sensitivity maximum of a photographic material in normal three wavelength regions of blue, green and red.

[0161] The exposure time in such a scanning exposure is defined as the time necessary to expose the size of the picture element (pixel) with the density of the picture element being 400 dpi, and preferred exposure time is 10^{-4} sec or less and more preferably 10^{-6} sec or less.

[0162] The scanning exposure system that can preferably be used in the present invention is described in detail in the patent publications shown in the above table.

[0163] With respect to the processing of the light-sensitive material of the present invention, processing materials (including details for color developing agents) and processing methods, as disclosed in JP-A-2-207250, from page 26, right under column, line 1 to page 34, right upper column, line 9, and JP-A-4-97355, from page 5, left upper column, line 17 to page 18, right under column, line 20, can be preferably applied, and these are incorporated herein by reference. Further, as preservatives which can be used in the developing solution, compounds described in the patent publications shown in the above table can be preferably used.

[0164] The present invention is preferably applied to a light-sensitive material having rapid processing suitability.

[0165] The term "color-developing time" as used herein refers to a period of time required from the beginning of dipping a light-sensitive material into a color-developing solution until the light-sensitive material is dipped into a blix solution in the subsequent processing step. in the case where a processing is carried out using, for example, an autoprocessor, the color-developing time is the sum total of a time in which a light-sensitive material has been dipped in a color-developing solution (so-called "time in the solution") and a time in which the light-sensitive material has been conveyed in air toward a bleach-fixing bath in the step subsequent to color development (so-called "time in the air"). Likewise, the term "blix time" as used herein refers to a period of time required from the beginning of dipping a light-sensitive material into a blix solution until the light-sensitive material is dipped into a washing bath or a stabilizing bath in the subsequent processing step. Further, the term "washing or stabilizing time" as used herein refers to a period of time required from the beginning of dipping a light-sensitive material into a washing solution or a stabilizing solution until the end of the dipping toward a drying step (so-called "time in the solution").

[0166] In the present invention, the color-developing time is preferably 60 sec or less, more preferably from 50 sec to 6 sec, further preferably from 30 sec to 6 sec. Likewise, the blix time is preferably 60 sec or less, more preferably from 50 sec to 6 sec, further preferably from 30 sec to 6 sec. Further, the washing or stabilizing time is preferably 150 sec or less, more preferably from 130 sec to 6 sec.

[0167] When the silver halide color photosensitive material of the present invention is a silver halide color photosensitive material having a reflective-type support (e.g. color paper), the following exposure and development systems can be mentioned: Automatic printing and development system described in JP-A-10-333253; Conveyor of light-sensitive materials, as described in JP-A-2000-10206; Recording system including an image-reading apparatus, as described in JP-A-11-215312; Exposure system including color image-recording system, as described in JP-A-11-88619 and JP-A-10-202950; Digital photo-printing system including remote diagnostic system, as described in JP-A-10-210206; and Photo-printing system including an image-recording apparatus, as described in JP-A-2000-310822.

[0168] In specific, those can be mentioned are, for example, Minilabo "PP350" (trade name) manufactured by Fuji Photo Film Co., Ltd., and, as a processing agent, CP48S Chemical, CP45X, or CP47L, manufactured by Fuji Photo Film Co., Ltd., or RA-100, RA-4, manufactured by Eastman Kodak Co., (each trade name).

[0169] Examples of a development method applicable to the light-sensitive material of the present invention after exposure, include a conventional wet system, such as a development method using a developing solution containing an alkali agent and a developing agent, and a development method wherein a developing agent is incorporated in the photographic material and an activator solution, e.g., a developing agent-free alkaline solution, is employed for the development, as well as a heat development system using no processing solution. In particular, the activator method is preferred over the other methods, because the processing solution contains no developing agent, thereby it enables easy management and handling of the processing solution, and reduction in waste disposal load to make for environmental preservation.

[0170] The preferable developing agents or their precursors to be incorporated in the photographic materials in the case of adopting the activator method include the hydrazine compounds described in, for example, JP-A-8-234388, JP-A-9-152686, JP-A-9-152693, JP-A-9-211814 and JP-A-9-160193.

[0171] Further, the processing method in which the light-sensitive material reduced in the amount of silver to be applied undergoes the image amplification processing using hydrogen peroxide (intensification processing), can be employed preferably. In particular, it is preferable to apply this processing method to the activator method. Specifically, the image-forming methods utilizing an activator solution containing hydrogen peroxide, as disclosed in JP-A-8-297354 and JP-A-9-152695 can be preferably used.

[0172] The processing with an activator solution is generally followed by a desilvering step in the activator method, but the desilvering step can be omitted in the case of applying the image amplification processing method to photographic materials of a low silver amount. In such a case, washing or stabilization processing can follow the processing with an activator solution to result in simplification of the processing process. On the other hand, when the system of reading the image information from photographic materials by means of a scanner or the like is employed, the processing form requiring no desilvering step can be applied, even if the photographic materials are those of a high silver amount, such as photographic materials for shooting.

[0173] The activator solution, desilvering solution (bleach-fixing solution), washing solution and stabilizing solution for use in the present invention can contain known ingredients and can be used in conventional manners. Preferably, those described in Research Disclosure, Item 36544, pp. 536-541 (September 1994), and JP-A-8-234388 can be used in the present invention.

[0174] The light-sensitive material of the present invention can be preferably used as a light-sensitive material for the advanced photo-system, which has a magnetic recording layer. The light-sensitive material of the present invention can be preferably used in a system wherein a small amount of water is used to perform heat-development, or in a complete dry system wherein no water is used to perform heat-development. Detailed descriptions on these systems are found, for example, in JP-A-6-35118, JP-A-6-17528, JP-A-56-146133, JP-A-60-119557, and JP-A-1-161236.

[0175] In the present invention, the wording "a silver halide photographic light-sensitive material" means to include not only a light-sensitive material for forming a color image but also a light-sensitive material for forming a monotone image, an example of which is a black and white image.

[0176] In case where the present invention is applied to a color paper, the light-sensitive material and the like described in JP-A-11-7109 are preferable, and particularly descriptions in paragraph numbers 0071 to 0087 in JP-A-11-7109 are preferable, and therefore the above descriptions in JP-A-11-7109 are incorporated herein by reference.

[0177] In case where the present invention is applied to a color negative film, the descriptions at paragraph Nos. 0115 to 0217 of the specification of JP-A-11-305396 can be preferably applied thereto, and therefore incorporated herein by reference.

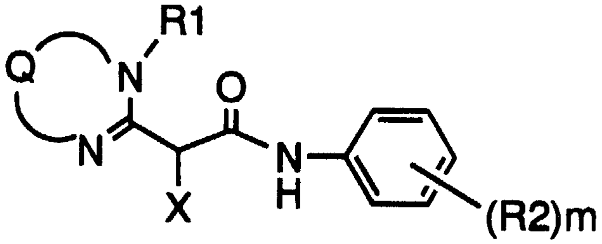
[0178] In case where the present invention is applied to a color reversal film, preferably to the light-sensitive material described in JP-A-2001-142181, and the descriptions at paragraph Nos. 0164 to 0188 of the specification of JP-A-2001-142181 and paragraphs Nos. 0018 to 0021 of the specification of JP-A-11-84601 can be preferably applied thereto, and therefore incorporated herein by reference.

[0179] In addition to the above, still another preferable embodiment of the present invention is:

(A) A silver halide color photographic light-sensitive material, having at least one blue-sensitive emulsion layer containing a yellow coupler, at least one green-sensitive emulsion layer containing a magenta coupler, and at least one red-sensitive emulsion layer containing a cyan coupler, on a support;

wherein said blue-sensitive emulsion layer contains at least one coupler represented by formula (I); and
wherein the silver halide color photographic light-sensitive material satisfies the following expression a-1) and/or b-1):

formula (I)



wherein, in formula (I), Q represents a group of non-metal atoms necessary to form a 5- to 7-membered ring together with the -N=C-N(R1)-; R1 represents a substituent; R2 represents a substituent; m represents 0 (zero) or an integer of 1 to 5; when m is 2 or more, R2s may be the same or different from each other, or R2s may bond together to form a ring; and X represents a hydrogen atom, or a group capable of being split-off upon a coupling reaction with an oxidized product of a developing agent;

$$\text{a-1)}: 0.5 \leqq \mathrm{Dmax(UV)/Dmin(UV)} \leqq 1.1$$

wherein Dmax(UV)/Dmin(UV) is the smallest value in a wavelength range of 340 nm or more and 450 nm or less, among values represented by (the maximum color density of yellow in a given wavelength)/(a density of an unexposed portion);

$$\text{b-1)}: 1300 \leqq \mathrm{(B-C)/A} \leqq 20000$$

wherein B represents the maximum color density of yellow, C represents the minimum color density of yellow, each of which means a transmission density when the support is a transmission support, or a reflection density when the support is a reflection support; A is an amount of the coupler represented by formula (I) to be used (mol/m^2).

[0180] According to the present invention, a silver halide photographic light-sensitive material that gives dyes excellent in hue and shows excellent color-forming property, and high-grade storability, whereby neither a white background portion nor a dye image portion become discolored or fade for a long time, can be provided at low cost. The silver halide photographic light-sensitive material of the present invention provides an image with little fog and color mixing, and it provides little reduction of the developed color density, even after long-term storage after coating as a raw stock; and it further provides excellent development processing stability.

[0181] The present invention will be explained in more detail by way of the following examples, but the invention is not intended to be limited thereto.

EXAMPLE

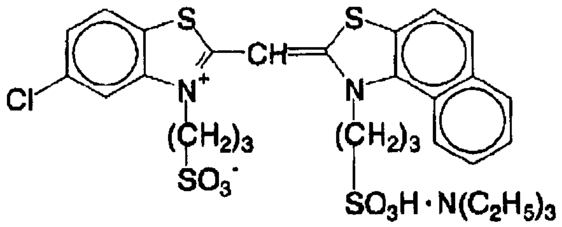
(Example 1)

(Preparation of Blue-sensitive Layer Emulsion A)

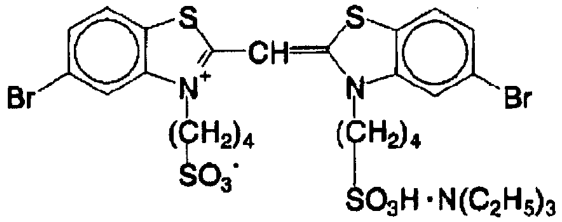
[0182] Silver halide cubic grains having a halide composition of 98.9 mol% of silver chloride, 1 mol% of silver bromide, and 0.1 mol% of silver iodide, and having the average side length of 0.70 μm with the variation coefficient of side length of 8%, were prepared. Spectral sensitizing dyes-1 and -2 were added thereto in an amount of 2.5 x 10^{-4} mole/mole of Ag and 2.0 x 10^{-4} mole/mole of Ag, respectively. At the step of grain formation, $K_3IrCl_5(H_2O)$, $K_4Ru(CN)_6$, $K_4Fe(CN)_6$, thiosulfonic acid compound-1, sodium thiosulfate, gold sensitizer-1, and mercapto compounds-1 and -2 were used in an optimal amount respectively. Thus, a high-sensitive emulsion A-1 was prepared.

[0183] Similarly, cubic grains having an average side length of 0.55 μm (variation coefficient of the side length, 9%) were prepared. Spectral sensitization and chemical sensitization were carried out in the same manner as the above, except for correcting the sensitization amounts so as to adjust the specific surface area (according to side length ratio 0.7/0.55=1.27 times). Thus, a low-sensitive emulsion A-2 was prepared.

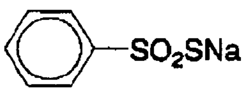
Spectral sensitizing dye - 1



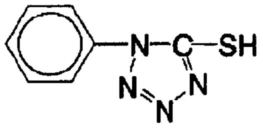
Spectral sensitizing dye - 2



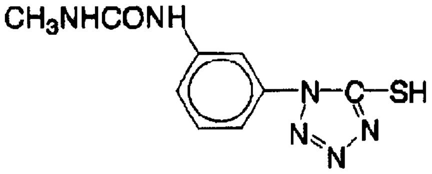
Thiosulfonic acid compound - 1



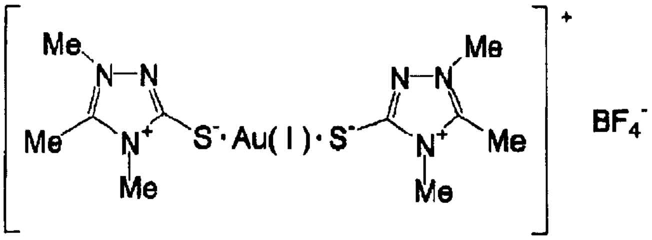
Mercapto compound - 1



Mercapto compound - 2



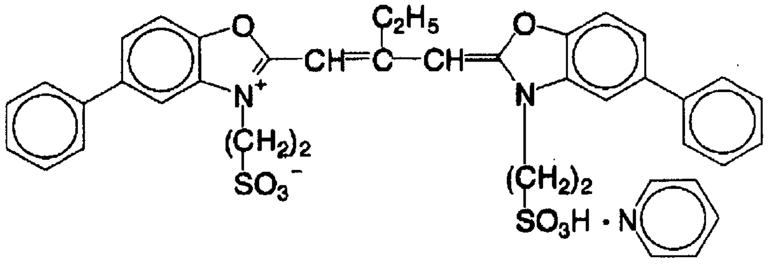
Gold sensitizer - 1



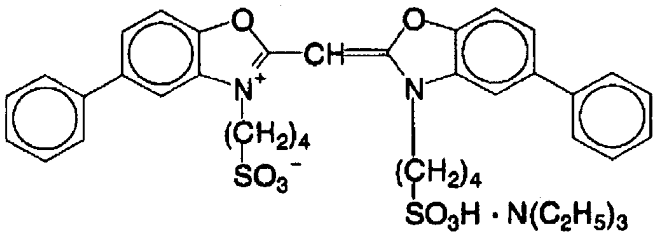
(Preparation of Green-sensitive Layer Emulsion C)

[0184] A high-sensitive green-sensitive emulsion C-1 and a low-sensitive green-sensitive emulsion C-2 were prepared in the same manner as Emulsion A-1 and Emulsion A-2 respectively, except that the temperature at the grain formation was lowered and kinds of the sensitizing dyes were changed as shown below.

(Sensitizing dye D)



(Sensitizing dye E)



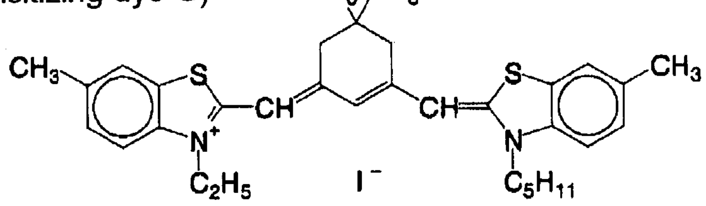
[0185] The grain size of the high-sensitive emulsion and the low-sensitive emulsion were 0.40 µm and 0.30 µm in terms of side length respectively. The variation coefficient of the side length in the emulsions was each 8%.

[0186] Sensitizing dye D was added to the large grain size emulsion in an amount of 3.0 x 10^{-4} mole, and to the small grain size emulsion in an amount of 3.6 x 10^{-4} mole, per mole of silver halide respectively. Further, sensitizing dye E was added to the large grain size emulsion in an amount of 4.0 x 10^{-5} mole, and to the small grain size emulsion in an amount of 7.0 x 10^{-5} mole, per mole of silver halide respectively.

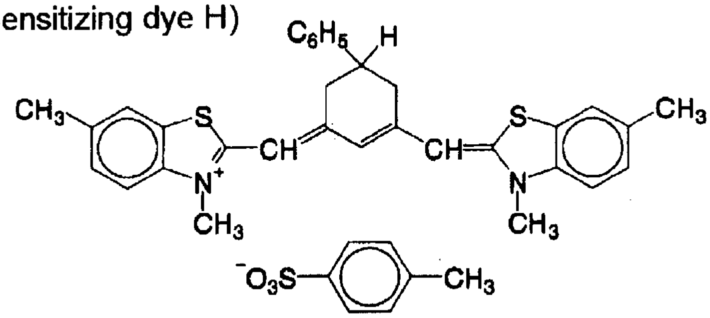
(Preparation of Red-sensitive Layer Emulsion E)

[0187] A high-sensitive red-sensitive emulsion E-1 and a low-sensitive red-sensitive emulsion E-2 were prepared in the same manner as Emulsion A-1 and Emulsion A-2 respectively, except that the temperature at the grain formation was lowered and kinds of the sensitizing dyes were changed as shown below.

(Sensitizing dye G)



(Sensitizing dye H)

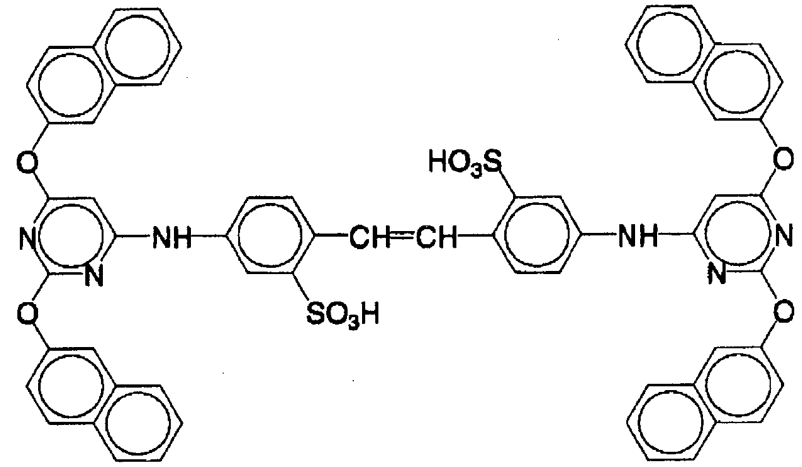


[0188] The grain size of the high-sensitive emulsion and the low-sensitive emulsion were 0.38 µm and 0.32 µm in terms of side length respectively. The variation coefficient of the side length in the emulsions was 9% and 10%, respectively.

[0189] Sensitizing dyes G and H were each added to the large grain size emulsion in an amount of 8.0 x 10^{-5} mole, and to the small grain size emulsion in an amount of 10.7 x 10^{-5} mole, per mole of silver halide respectively.

[0190] Further, the following compound I was added to the red-sensitive emulsion layer, in an amount of 3.0 x 10^{-3} mole, per mole of silver halide.

(Compound I)



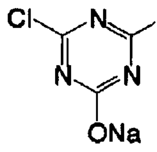
Preparation of Coating Solution for First Layer

[0191] 49 g of a yellow coupler (exemplified coupler (27)) was dissolved in 49 g of a solvent (Solv-9) and 10 ml of ethyl acetate. This solution was emulsified and dispersed with a high velocity stirring emulsifier (dissolver) in 220 g of a 23.5 mass% aqueous gelatin solution containing 4 g of sodium dodecylbenzene sulfonate, and water was added thereto to obtain 900 g of Emulsified Dispersion A.

[0192] On the other hand, the above-described Emulsified Dispersion A and the above-described Emulsion A-1 and Emulsion A-2 were mixed and dissolved, to prepare a coating solution for the first layer having the composition shown below. The coating amount of the emulsion is indicated in terms of silver.

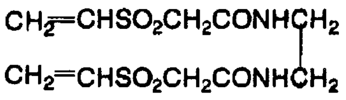
[0193] The coating solutions for the second to seventh layers were prepared in the same manner as the coating solution for the first layer. 1-Oxy-3,5-dichloro-s-triazine sodium salts (H-1), (H-2), and (H-3) were used as gelatin hardening agents in each layer. Further, (Ab-1), (Ab-2), (Ab-3), and (Ab-4) were added to each layer such that their total amounts became 15.0 mg/m^2, 60.0 mg/m^2, 5.0 mg/m^2 and 10.0 mg/m^2, respectively.

(H − 1) Hardener



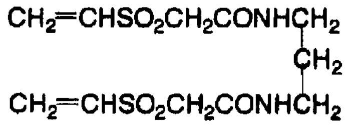
(used in an amount 1.4 mass% per gelatin)

(H − 2) Hardener



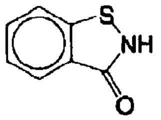
$$\begin{array}{l} CH_2{=}CHSO_2CH_2CONHCH_2 \\ CH_2{=}CHSO_2CH_2CONHCH_2 \end{array}$$

(H − 3) Hardener

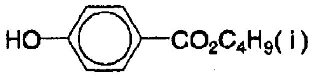


$$\begin{array}{l} CH_2{=}CHSO_2CH_2CONHCH_2 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad CH_2 \\ \qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CHSO_2CH_2CONHCH_2 \end{array}$$

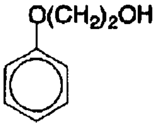
(A b − 1) Antiseptic



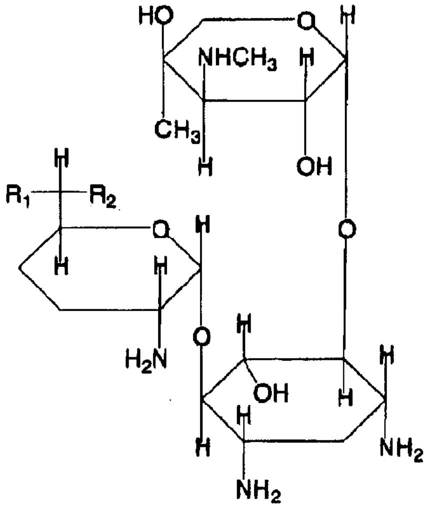
(A b − 2) Antiseptic



(A b − 3) Antiseptic



(A b − 4) Antiseptic



	R_1	R_2
a	$-CH_3$	$-NHCH_3$
b	$-CH_3$	$-NH_2$
c	$-H$	$-NH_2$
d	$-H$	$-NHCH_3$

A mixture in 1:1:1:1 (molar ratio) of a, b, c, and d

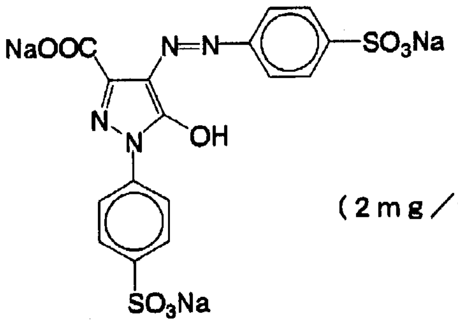
[0194] Further, 1-(3-methylureidophenyl)-5-mercaptotetrazole was added to the second layer, the fourth layer, the sixth layer, and the seventh layer, in an amount of 0.2 mg/m^2, 0.2 mg/m^2, 0.6 mg/m^2, 0.1 mg/m^2, respectively.

[0195] Further, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added to the blue-sensitive emulsion layer and the green-sensitive emulsion layer, in respective amounts of 1 x 10^{-4} mole and 2 x 10^{-4} mole, per mole of silver halide.

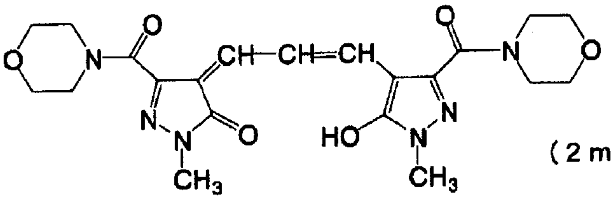
[0196] Further, to the red-sensitive emulsion layer, added was a latex of a copolymer of methacrylic acid and butyl acrylate (mass ratio 1:1, average molecular weight 200,000 to 400,000) in an amount of 0.05 g/m^2.

[0197] Further, disodium catechol-3,5-disulfonate was added to the second layer, the fourth layer, and the sixth layer, in respective amounts of 6 mg/m^2, 6 mg/m^2, and 18 mg/m^2.

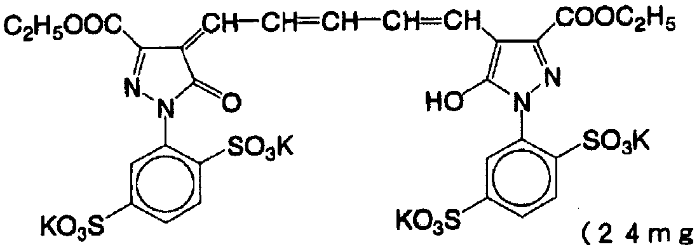
[0198] Further, in order to prevent irradiation, the following dyes were added. The numerals in the parentheses indicate a coating amount.



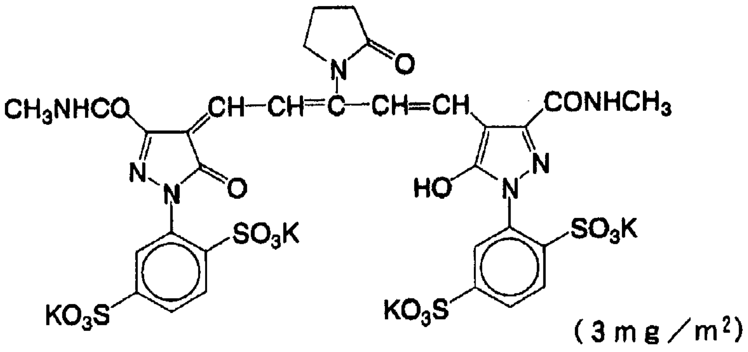
(2 mg/m^2)



(2 mg/m^2)



(24 mg/m^2)



(Layer Constitution)

[0199] The composition of each layer is shown below. The numbers show coating amounts (g/m^2). In the case of a silver halide emulsion, the coating amount is in terms of silver.

Support

[0200] Polyethylene resin laminated paper {The polyethylene resin on the first layer side contained a white pigment (TiO_2, content of 16 mass%; ZnO, content of 4 mass%), a fluorescent whitening agent (4,4'-bis(5-methylbenzoxazolyl) stilbene, content of 0.03 mass%) and a bluish dye (ultramarine, content of 0.33 mass%), the amount of polyethylene resin was 29.2 g/m^2}

First Layer (Blue-Sensitive Emulsion Layer)	
A silver chlorobromoiodide emulsion A (gold and sulfur sensitized, cubic, a 3:7 mixture of the large-size emulsion A-1 and the small-size emulsion A-2 (in terms of mol of silver))	0.15
Gelatin	1.10
Yellow coupler (Exemplified Coupler (27))	0.49
Solvent (Solv-9)	0.49
Second Layer (Color-Mixing Inhibiting Layer)	
Gelatin	1.15
Color-mixing inhibitor (Cpd-4)	0.10
Color-image stabilizer (Cpd-5)	0.018
Color-image stabilizer (Cpd-6)	0.13
Color-image stabilizer (Cpd-7)	0.07
Solvent (Solv-1)	0.04
Solvent (Solv-2)	0.12
Solvent (Solv-5)	0.11

Third Layer (Green-Sensitive Emulsion Layer)	
A silver chlorobromoiodide emulsion C (gold and sulfur sensitized, cubic, a 1:3 mixture of the large-size emulsion C-1 and the small-size emulsion C-2 (in terms of mol of silver))	0.14
Gelatin	1.21
Magenta coupler (ExM)	0.15
Ultraviolet absorbing agent (UV-A)	0.14
Color-image stabilizer (Cpd-2)	0.003
Color-image stabilizer (Cpd-4)	0.002

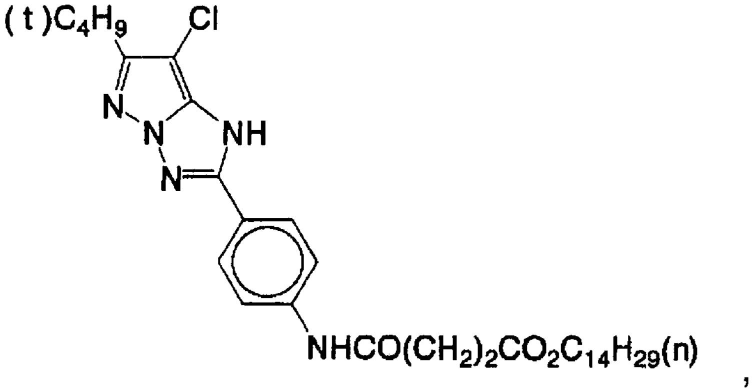
(continued)

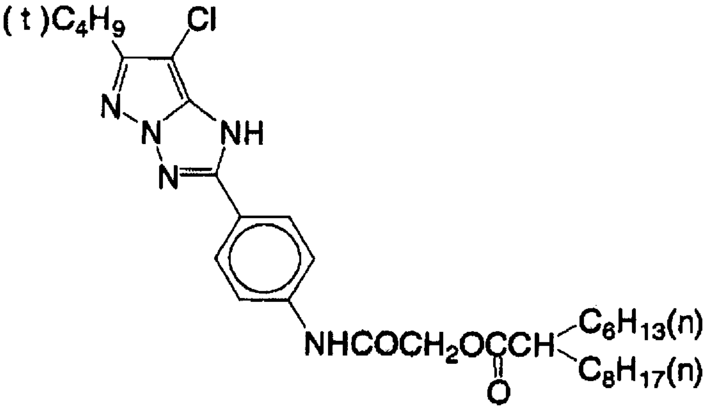
Third Layer (Green-Sensitive Emulsion Layer)	
Color-image stabilizer (Cpd-6)	0.09
Color-image stabilizer (Cpd-8)	0.02
Color-image stabilizer (Cpd-9)	0.01
Color-image stabilizer (Cpd-10)	0.01
Color-image stabilizer (Cpd-11)	0.0001
Solvent (Solv-3)	0.09
Solvent (Solv-4)	0.18
Solvent (Solv-5)	0.17
Fourth Layer (Color-Mixing Inhibiting Layer)	
Gelatin	0.68
Color-mixing inhibitor (Cpd-4)	0.06
Color-image stabilizer (Cpd-5)	0.011
Color-image stabilizer (Cpd-6)	0.08
Color-image stabilizer (Cpd-7)	0.04
Solvent (Solv-1)	0.02
Solvent (Solv-2)	0.07
Solvent (Solv-5)	0.065

Fifth Layer (Red-Sensitive Emulsion Layer)	
A silver chlorobromoiodide emulsion E (gold and sulfur sensitized, cubic, a 5:5 mixture of the large-size emulsion E-1 and the small-size emulsion E-2 (in terms of mol of silver))	0.16
Gelatin	0.95
Cyan coupler (ExC-1)	0.023
Cyan coupler (ExC-2)	0.05
Cyan coupler (ExC-3)	0.17
Ultraviolet absorbing agent (UV-A)	0.055
Color-image stabilizer (Cpd-1)	0.22
Color-image stabilizer (Cpd-7)	0.003
Color-image stabilizer (Cpd-9)	0.01
Color-image stabilizer (Cpd-12)	0.01
Solvent (Solv-8)	0.05
Sixth Layer (Ultraviolet Absorbing Layer)	
Gelatin	0.46
Ultraviolet absorbing agent (UV-B)	0.35
Compound (S1-4)	0.0015
Solvent (Solv-7)	0.18
Seventh Layer (Protective Layer)	
Gelatin	1.00
Acryl-modified copolymer of polyvinyl alcohol (modification degree: 17%)	0.4
Liquid paraffin	0.02
Surface-active agent (Cpd-13)	0.02

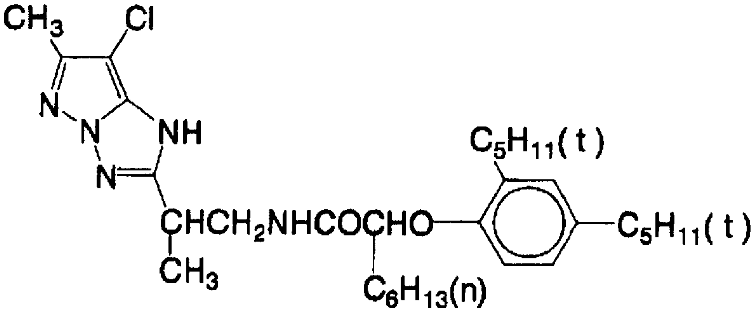
(ExM) Magenta coupler

A mixture in 40:40:20 (molar ratio) of

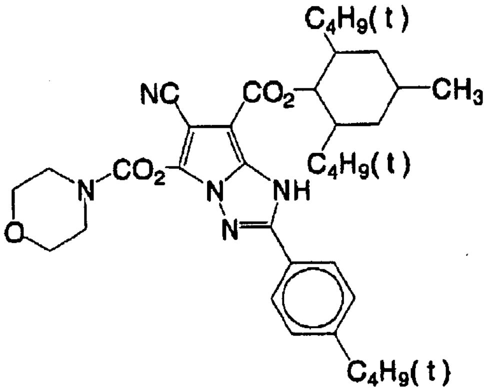




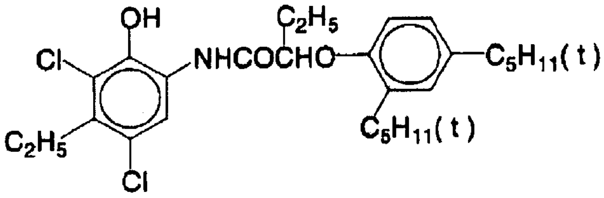
and



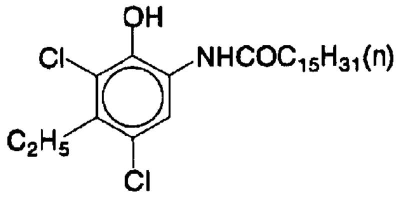
(E x C − 1) Cyan coupler



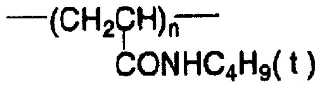
(E x C − 2) Cyan coupler



(E x C − 3) Cyan coupler



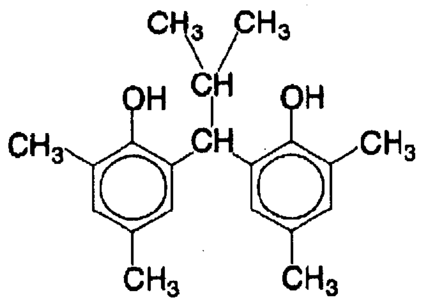
(Cpd-1) Color-image stabilizer



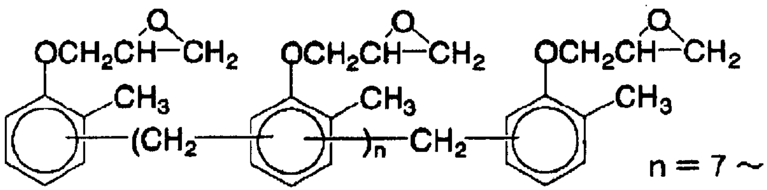
$-(CH_2\underset{|}{C}H)_n-$ with $CONHC_4H_9(t)$ below: $$-(CH_2\underset{CONHC_4H_9(t)}{CH})_n-$$

number-average molecular weight 60,000

(Cpd-2) Color-image stabilizer

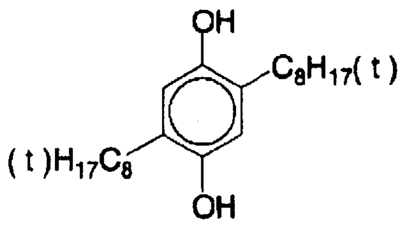


(Cpd-3) Color-image stabilizer

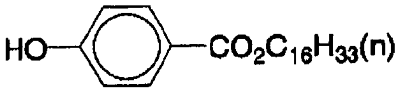


n = 7 ~ 8 (average value)

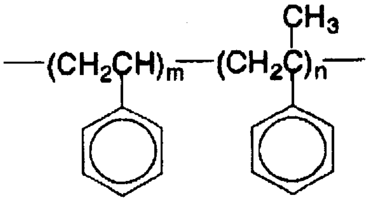
(Cpd-4) Color-mixing inhibitor



(Cpd−5) Color-image stabilizer



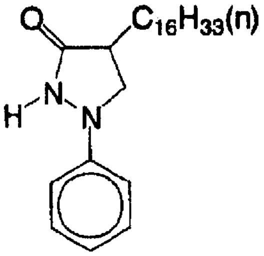
(Cpd−6) Color-image stabilizer



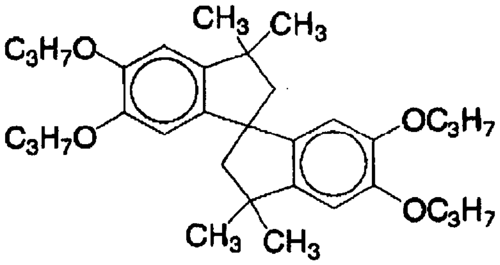
number-average molecular weight 600

m／n＝10／90

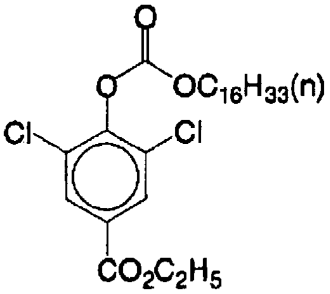
(Cpd−7)
Color-image stabilizer



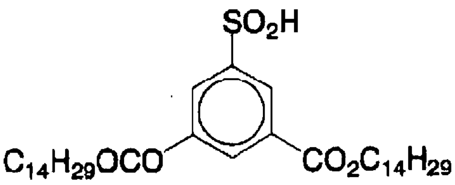
(Cpd−8)
Color-image stabilizer



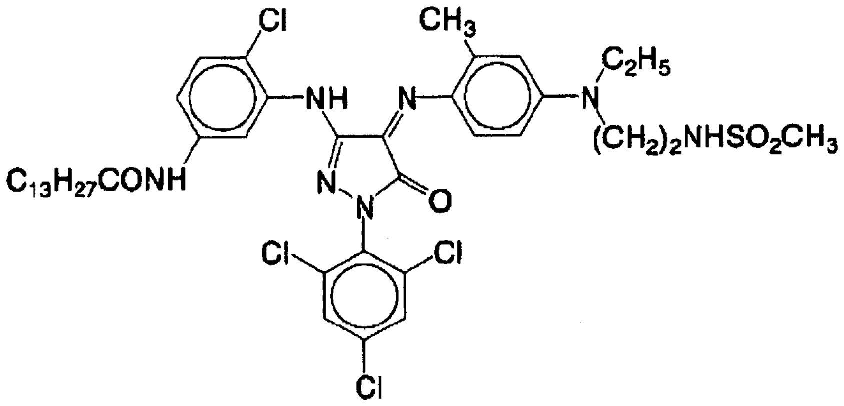
(Cpd−9)
Color-image stabilizer



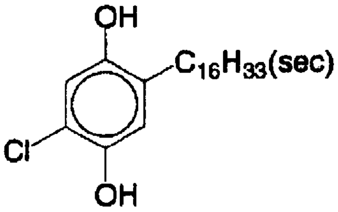
(Cpd−10)
Color-image stabilizer



(Cpd−11)

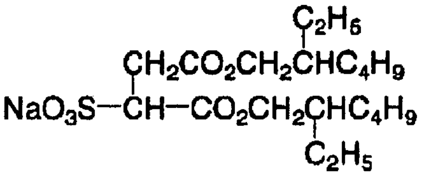


(Cpd−12)



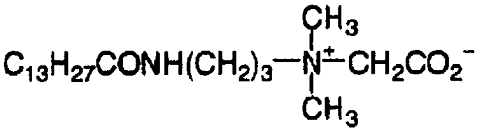
(Cpd−13) Surface-active agent

A mixture in 7:3 (molar ratio) of



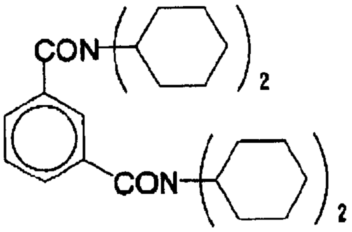
$$\mathrm{NaO_3S{-}\overset{\displaystyle CH_2CO_2CH_2\overset{\displaystyle C_2H_5}{\overset{|}{C}}HC_4H_9}{\overset{|}{C}H}{-}CO_2CH_2\underset{\underset{\displaystyle C_2H_5}{|}}{C}HC_4H_9}$$

and

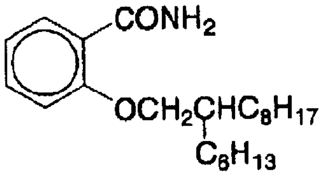


$$\mathrm{C_{13}H_{27}CONH(CH_2)_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\pm}}}}{-}CH_2CO_2^-}$$

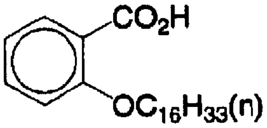
(Cpd－14)



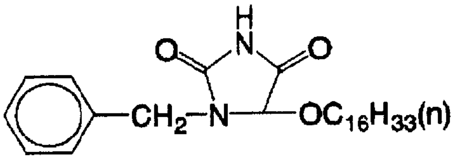
(Cpd－15)



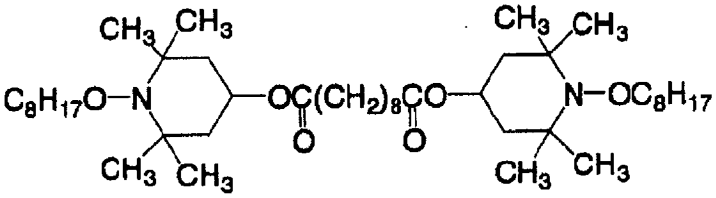
(Cpd－16)



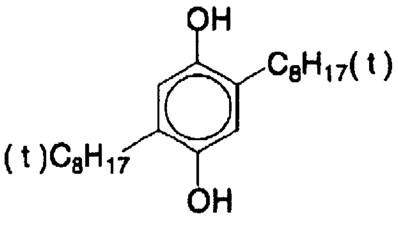
(Cpd－17)



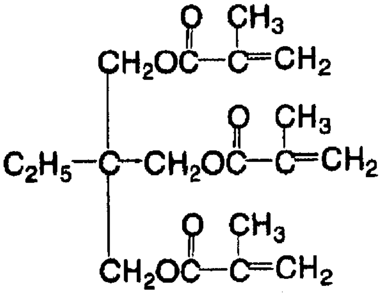
(Cpd－18)



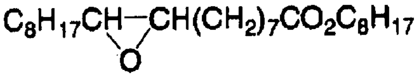
(Cpd－19)
Color-mixing inhibitor



(Cpd－20)

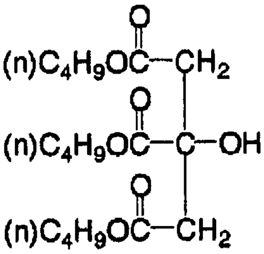


(Solv−1)

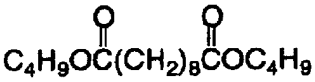


$C_8H_{17}CH\overset{}{-}CH(CH_2)_7CO_2C_8H_{17}$ (epoxide: $\underset{O}{\diagdown\diagup}$)

(Solv−2)



(Solv−3)

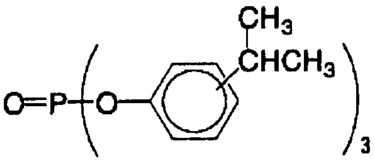


$C_4H_9O\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OC_4H_9$

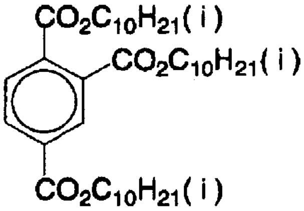
(Solv−4)

$O{=}P(OC_6H_{13}(n))_3$

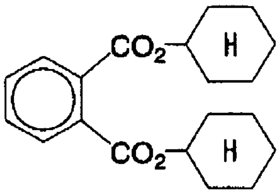
(Solv−5)



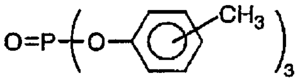
(Solv−7)



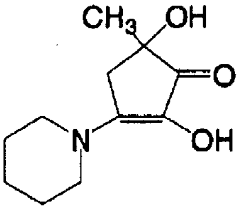
(Solv−8)



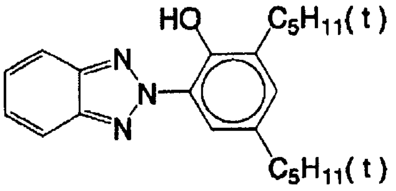
(Solv−9)



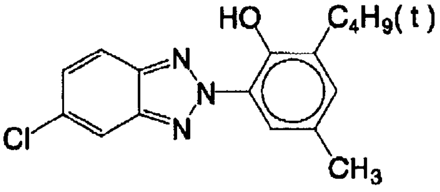
(S1−4)



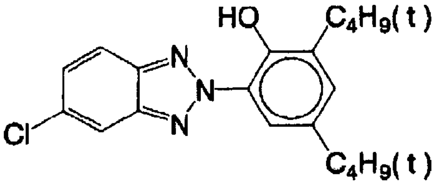
(UV－1)
Ultraviolet absorbing agent



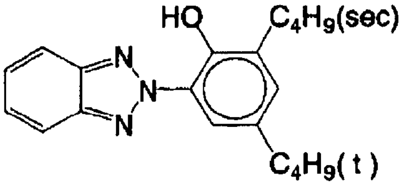
(UV－2)
Ultraviolet absorbing agent



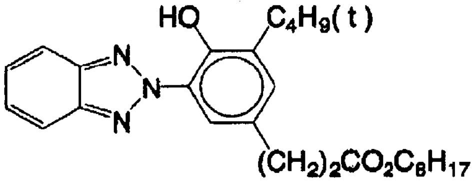
(UV－3)
Ultraviolet absorbing agent



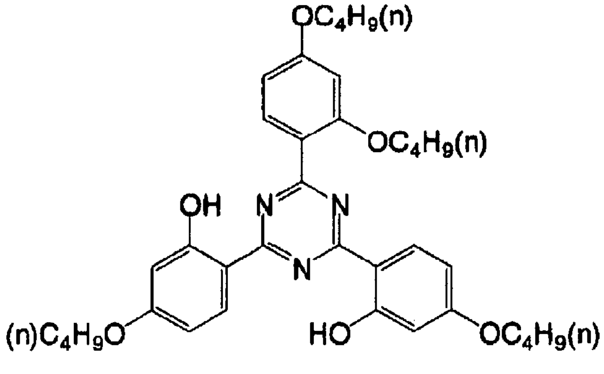
(UV－5)
Ultraviolet absorbing agent



(UV－6) Ultraviolet absorbing agent



(UV－7) Ultraviolet absorbing agent



UV-A : A mixture of UV-1/UV-2/UV-3=7/2/2 (mass ratio)
UV-B : A mixture of UV-1/UV-2/UV-3/UV-5/UV-6=13/3/3/5/3 (mass ratio)
UV-C : A mixture of UV-1/UY-3=9/1 (mass ratio)

[0201] Samples 102 to 120 were prepared in the same manner as in the above-mentioned preparation of the sample 101, except that the composition of the first layer was changed as shown in Table 2.

[0202] The yellow coupler in each sample was changed so as to become an equimolar amount to the yellow coupler in the sample 101. In the samples, in which the compound according to the present invention was used, the amount of the solvent (Solv-1) was reduced in an amount corresponding to the amount (mass) of the compound added.

[0203] The above-described light-sensitive material sample 102 was processed to a 127-mm width roll-like form. Mini-lab printer processor PP350 (trade name) manufactured by Fuji Photo Film Co., Ltd. was used to subject the light-sensitive material sample to image-wise exposure through a negative film having an average density. A continuous processing (running test) was performed until an accumulated replenisher amount of color developer in the processing steps presented below reached two times the tank volume of a color developer. The following two processings, which were different in the composition of processing solutions and processing time, were carried out, to evaluate the light-sensitive materials.

Processing Step A

[0204] A processing with the following running processing solution was named processing A.

Processing step	Temperature	Time	Replenisher amount*
Color development	38.5 °C	45 sec	45 ml
Bleach-fixing	38.0 °C	45 sec	35 ml
Rinse (1)	38.0 °C	20 sec	-
Rinse (2)	38.0 °C	20 sec	-
Rinse (3)**	38.0 °C	20 sec	-
Rinse (4)**	38.0 °C	20 sec	121 ml
Drying	80 °C		

(Note)
* Replenisher amount per m^2 of the light-sensitive material to be processed.
** A rinse cleaning system RC50D (trade name), manufactured by Fuji Photo Film Co., Ltd., was installed in the rinse (3), and the rinse solution was taken out from the rinse (3) and sent to a reverse osmosis membrane module (RC50D) by using a pump. The permeated water obtained in that tank was supplied to the rinse (4), and the concentrated water was returned to the rinse (3). Pump pressure was controlled such that the water to be permeated in the reverse osmosis module would be maintained in an amount of 50 to 300 ml/min, and the rinse solution was circulated under controlled temperature for 10 hours a day. The rinse was made in a tank counter-current system from (1) to (4).

[0205] The composition of each processing solution was as follows.

(Color developer)	(Tank solution)	(Replenisher)
Water	800 ml	800 ml
Fluorescent whitening agent (FL-1)	2.2 g	5.1 g
Fluorescent whitening agent (FL-2)	0.35 g	1.75 g
Triisopropanolamine	8.8 g	8.8 g
Polyethylenegrycol (average molecular weight: 300)	10.0 g	10.0 g
Ethylenediamine tetraacetic acid	4.0 g	4.0 g
Sodium sulfite	0.10 g	0.20 g
Potassium chloride	10.0 g	-
Sodium 4,5-dihydroxybenzene -1,3-disulfonate	0.50 g	0.50 g
Disodium-N,N-bis(sulfonatoethyl) hydroxylamine	8.5 g	14.0 g
4-amino-3-methyl-N-ethyl-N -(β-methanesulfonamidoethyl) aniline · 3/2 sulfate · monohydrate	4.8 g	14.0 g
Potassium carbonate	26.3 g	26.3 g
Water to make	1000 ml	1000 ml
pH (25 °C/adjusted using sulfuric acid and KOH)	10.15	10.25

(Bleach-fixing solution)	(Tank solution)	(Replenisher)
Water	800 ml	800 ml
Ammonium thiosulfate (750 g/l)	107 ml	214 ml
m-Carboxymethylbenzenesulfinic acid	8.3 g	16.5 g
Ammonium iron (III) ethylenediaminetetraacetate	47.0 g	94.0 g
Ethylenediamine tetraacetic acid	1.4 g	2.8 g

(continued)

(Bleach-fixing solution)	(Tank solution)	(Replenisher)
Nitric acid (67%)	16.5 g	33.0 g
Imidazole	14.6 g	29.2 g
Ammonium sulfite	16.0 g	32.0 g
Potassium metabisulfite	23.1 g	46.2 g
Water to make	1000 ml	1000 ml
pH (25 °C/adjusted using nitric acid and aqua ammonia)	6.5	6.5

(Rinse solution)	(Tank solution)	(Replenisher)
Sodium chlorinated-isocyanurate	0.02 g	0.02 g
Deionized water (conductivity: 5 μS/cm or less)	1000 ml	1000 ml
PH (25 °C)	6.5	6.5

Processing Step B

[0206] The above-described light-sensitive material sample 102 was processed to a 127-mm width roll-like form. Mini-lab printer processor PP350 (trade name) manufactured by Fuji Photo Film Co., Ltd. was used to subject the light-sensitive material sample to image-wise exposure through a negative film having an average density. A continuous processing (running test) was performed until an accumulated replenisher amount of color developer in the processing steps presented below reached two times the tank volume of a color developer. The processing with the resulting running processing solution was named processing B.

Processing step	Temperature	Time	Replenisher amount*
Color development	45.0 °C	20 sec	45 ml
Bleach-fixing	40.0 °C	20 sec	35 ml
Rinse (1)	40.0 °C	8 sec	-
Rinse (2)	40.0 °C	8 sec	-
Rinse (3)**	40.0 °C	8 sec	-
Rinse (4)**	38.0 °C	8 sec	121 ml
Drying	80 °C	15 sec	

(Note)
* Replenisher amount per m^2 of the light-sensitive material to be processed.

** A rinse cleaning system RC50D (trade name), manufactured by Fuji Photo Film Co., Ltd., was installed in the rinse (3), and the rinse solution was taken out from the rinse (3) and sent to a reverse osmosis membrane module (RC50D) by using a pump. The permeated water obtained in that tank was supplied to the rinse (4), and the concentrated water was returned to the rinse (3). Pump pressure was controlled such that the water to be permeated in the reverse osmosis module would be maintained in an amount of 50 to 300 ml/min, and the rinse solution was circulated under controlled temperature for 10 hours a day. The rinse was made in a tank counter-current system from (1) to (4).

[0207] The composition of each processing solution was as follows.

(Color developer)	(Tank solution)	(Replenisher)
Water	800 ml	800 ml
Fluorescent whitening agent (FL-3)	4.0 g	8.0 g
Residual color reducing agent (SR-1)	3.0 g	5.5 g
Triisopropanolamine	8.8 g	8.8 g
Sodium p-toluenesulfonate	10.0 g	10.0 g
Ethylenediamine tetraacetic acid	4.0 g	4.0 g
Sodium sulfite	0.10 g	0.10 g
Potassium chloride	10.0 g	-
Sodium 4,5-dihydroxybenzene -1,3-disulfonate	0.50 g	0.50 g
Disodium-N,N-bis(sulfonatoethyl) hydroxylamine	8.5 g	14.0 g

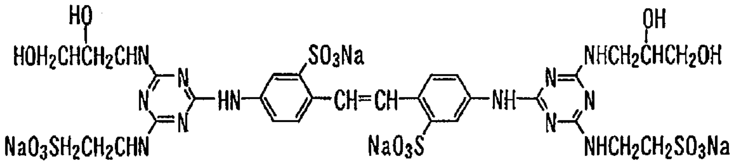
(continued)

(Color developer)	(Tank solution)	(Replenisher)
4-Amino-3-methyl-N-ethyl-N -(β-methanesulfonamidoethyl) aniline· 3/2 sulfate·monohydrate	7.0 g	19.0 g
Potassium carbonate	26.3 g	26.3 g
Water to make	1000 ml	1000 ml
pH (25 °C/adjusted using sulfuric acid and potassium hydroxide)	10.25	12.6

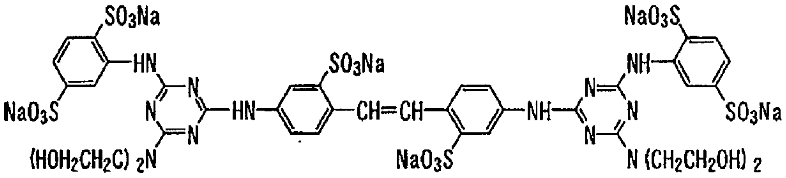
(Bleach-fixing solution)	(Tank solution)	(Replenisher)
Water	800 ml	800 ml
Ammonium thiosulfate (750 g/l)	107 ml	214 ml
Succinic acid	29.5 g	59.0 g
Ammonium iron (III) ethylenediaminetetraacetate	47.0 g	94.0 g
Ethylenediamine tetraacetic acid	1.4 g	2.8 g
Nitric acid (67%)	17.5 g	35.0 g
Imidazole	14.6 g	29.2 g
Ammonium sulfite	16.0 g	32.0 g
Potassium metabisulfite	23.1 g	46.2 g
Water to make	1000 ml	1000 ml
pH (25 °C/adjusted using nitric acid and aqua ammonia)	6.00	6.00

(Rinse solution)	(Tank solution)	(Replenisher)
Sodium chlorinated-isocyanurate	0.02 g	0.02 g
Deionized water (conductivity: 5 µS/cm or less)	1000 ml	1000 ml
PH (25 °C)	6.5	6.5

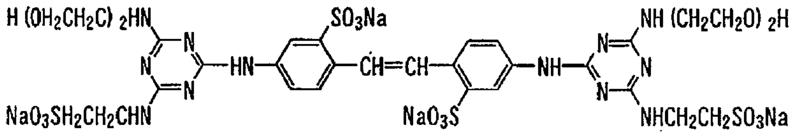
FL-1



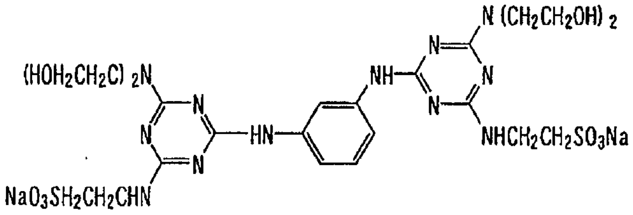
FL-2



FL-3



SR-1



[0208] After keeping samples 101 to 120 under conditions of 25 °C and 55%RH for 10 days after coating of the light-sensitive materials, the following evaluation was performed.

(Evaluation 1: Fastness to light)

[0209] Each sample was subjected to exposure for a blue separation using a sensitometer through a band pass filter of 465 nm and an optical wedge for an exposure time of 1/10000 seconds. After exposure, each sample was processed according to the above-mentioned processing step B. The yellow density after irradiation to a 100,000-lux xenon light for 6 days, at a portion where the initial yellow density was 0.5 before irradiation to light, was measured, to evaluate the fastness to light. The fastness to light was indicated by a remaining rate (%) of the density.

[0210] The results of the fastness to light are shown in Table 2.

[0211] Note that, in Table 2, the symbol "Cp" means a coupler, and the amount of the compound in the table is indicated by a mole% based on the yellow coupler. These indications are used hereinafter also in Tables 3 and 5.

Table 2

Sample No.	Yellow coupler	Compound of this invention		Fastness to light (Density remaining rate%)	Remarks
		Kind	Amount (mol% vs Cp)		
101	(27)	-	0	68	Comparative Example
102	(27)	TI-7	30	73	This invention
103	(27)	TI-8	30	74	This invention
104	(27)	TI-34	30	73	This invention
105	(27)	TI-24	30	77	This invention
106	(27)	TI-57	30	77	This invention
107	(27)	TI-58	30	76	This invention
108	(27)	TI-10	30	74	This invention
109	(27)	TIII-1	30	72.5	This invention
110	(27)	TIV-2	30	75	This invention
111	(27)	TV-14	30	73	This invention

Table 2 (continued)

Sample No.	Yellow coupler	Compound of this invention		Fastness to light (Density remaining rate%)	Remarks
		Kind	Amount (mol% vs Cp)		
112	(27)	TVI-12	30	73	This invention
113	(27)	TVI-21	30	75	This invention
114	(27)	TVII-3	30	72.5	This invention
115	(21)	-	0	64	Comparative Example
116	(21)	TI-8	30	75	This invention
117	(21)	TI-24	30	73	This invention
118	(30)	-	0	69	Comparative Example
119	(30)	TI-8	30	74	This invention
120	(30)	TI-24	30	78	This invention

[0212] As is apparent from Table 2, the use of the compounds according to the present invention, in combination with the yellow couplers according to the present invention, improved the fastness to light.

[0213] Further, it was confirmed that all the samples according to the present invention were less deteriorated in color-forming property, even after they were stored under conditions of 25 °C and relative humidity of 55% after coating of photographic layers.

(EXAMPLE 2)

[0214] Samples 201 to 220 were prepared in the same manner as Sample 101 in Example 1, except that the composition of the first layer was changed as shown in Table 3.

[0215] After keeping Samples 201 to 220 under the conditions of 25 °C and 55%RH for 10 days after coating of the light-sensitive material, the fastness property to light was evaluated. The evaluation was carried out according to that in Example 1, except that the processing step was changed to the processing step A. The results are shown in Table 3.

Table 3

Sample No.	Yellow coupler	Compound of this invention		Fastness to light (Density remaining rate %)	Remarks
		Kind	Amount (mol%vsCp)		
201	(27)	-	0	68	Comparative Example
202	(27)	TI-8	30	74	This invention
203	(27)	TI-8	60	74	This invention
204	(27)	TI-57	30	77	This invention
205	(27)	TI-57	60	76	This invention
206	(27)	TI-24	30	77	This invention
207	(27)	TI-24	60	77	This invention
208	(27)	TVI-21	30	75	This invention
209	(27)	TVI-21	60	75	This invention
210	(27)	TI-8 TI-24	30 30	81	This invention

Table 3 (continued)

Sample No.	Yellow coupler	Compound of this invention		Fastness to light (Density remaining rate %)	Remarks
		Kind	Amount (mol%vsCp)		
211	(27)	TI-8 TI-57	30 30	81	This invention
212	(27)	TI-8 TI-24 TVI-21	30 30 30	83	This invention
213	(27)	TI-57 TI-24 TVI-21	30 30 30	83	This invention
214	(30)	-	0	69	Comparative Example
215	(30)	TI-8	30	74	This invention
216	(30)	TI-8	60	74	This invention
217	(30)	TI-24	30	78	This invention
218	(30)	TI-24	60	78	This invention
219	(30)	TI-8 TI-24	30 30	82	This invention
220	(30)	TI-8 TI-24 TVI-21	30 30 30	84	This invention

[0216] The results in Table 3 show that light-fading was siginificantly suppressed in the samples, in which the compound represented by formula (TS-IB) and the compound represented by formula (TS-IG) or (TS-IE) according to the present invention were used in combination, to the level to which the sample, in which one of the compounds was used singly, could not reach. Further, it is apparent that the effect became larger when the compound represented by formula (TS-VI) was used in addition to the above-described compounds.

(EXAMPLE 3)

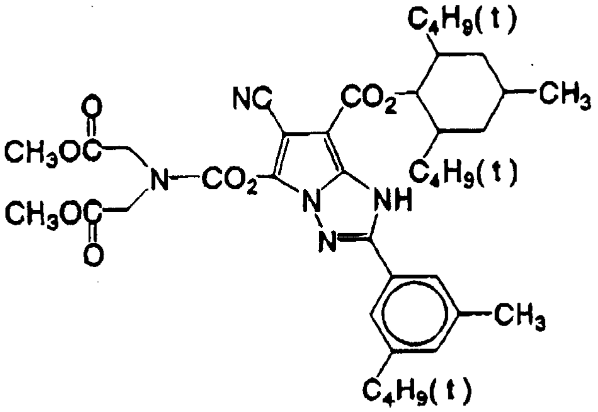
[0217] Samples were prepared in the same manner as in Examples 1 and 2, except that the composition of the fifth layer was changed as follows. Then, evaluations according to Examples 1 and 2 were carried out, and it was confirmed that samples that had the constitution according to the present invention also reproduced excellent fastness to light.

Fifth Layer (Red-Sensitive Emulsion Layer) A silver chlorobromoiodide emulsion E (gold and sulfur sensitized, cubic, a 5:5 mixture of the large-size emulsion E-1 and the small-size emulsion E-2 (in terms of mol of silver))	0.10
Gelatin	1.11
Cyan coupler (ExC-1)	0.02
Cyan coupler (ExC-3)	0.01
Cyan coupler (ExC-4)	0.11
Cyan coupler (ExC-5)	0.01
Color-image stabilizer (Cpd-1)	0.01
Color-image stabilizer (Cpd-6)	0.06
Color-image stabilizer (Cpd-7)	0.02
Color-image stabilizer (Cpd-9)	0.04
Color-image stabilizer (Cpd-10)	0.01
Color-image stabilizer (Cpd-14)	0.01

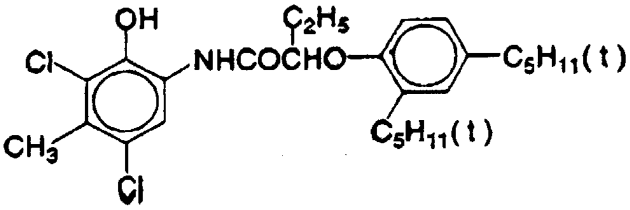
(continued)

Color-image stabilizer (Cpd-15)	0.12
Color-image stabilizer (Cpd-16)	0.01
Color-image stabilizer (Cpd-17)	0.01
Color-image stabilizer (Cpd-18)	0.07
Color-image stabilizer (Cpd-20)	0.01
Ultraviolet absorbing agent (UV-7)	0.01
Solvent (Solv-5)	0.15

(ExC-4) Cyan coupler



(ExC-5) Cyan coupler



(EXAMPLE 4)

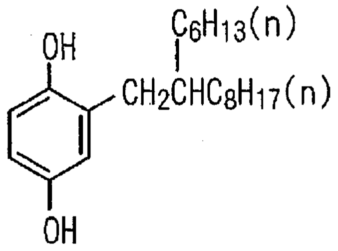
[0218] Sample 401 was prepared in the same manner as sample 109 described in Example 1 of JP-A-2001-142181, except that the composition of each of the 15th layer, the 16th layer, and 17th layer was changed as described below, respectively.

15th layer (low-sensitive blue-sensitive emulsion layer)	
Silver iodobromide emulsion L	
Silver amount	0.11
Silver iodobromide emulsion M	
Silver amount	0.15
Gelatin	0.80
Yellow coupler (Exemplified coupler (45))	0.30

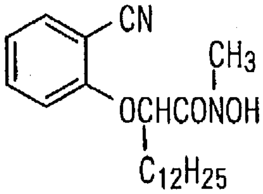
(continued)

15th layer (low-sensitive blue-sensitive emulsion layer)	
Compound Cpd-M	0.01
High boiling point organic solvent (tricresyl phosphate)	0.05
16th layer (low-sensitive layer)blue-sensitive emulsion	
Silver iodobromide emulsion N	
Silver amount	0.15
Silver iodobromide emulsion O	
Silver amount	0.15
Gelatin	0.76
Yellow coupler (Exemplified coupler (45))	0.34
Compound Cpd-N	0.002
High boiling point organic solvent (tricresyl phosphate)	0.06
17th layer (low-sensitive layer)blue-sensitive emulsion	
Silver iodobromide emulsion O	
Silver amount	0.15
Silver iodobromide emulsion P	
Silver amount	0.15
Gelatin	1.10
Yellow coupler (Exemplified coupler (45))	0.92
Compound Cpd-N	0.005
Compound Cpd-Q	0.20
High boiling point organic solvent (tricresyl phosphate)	0.17

Cpd-M



Cpd-N



Cpd-Q

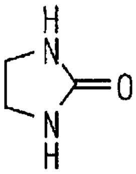


Table 4

Emulsions used in the samples				
Emulsion	Characteristic	Sphere equivalent average grain diameter (μm)	Variation coefficient (%)	Content of AgI (%)
L	Monodisperse tetradecahedral grain	0.33	10	4.5
M	Monodisperse cubic grain	0.33	9	6.0
N	Monodisperse cubic grain	0.43	9	2.5
O	Monodisperse tabular grain having {111} plane and average aspect ratio of 6.0	0.75	9	3.0
P	Monodisperse tabular grain having {111} plane and average aspect ratio of 6.0	0.90	8	2.8

[0219] Samples 402 to 408 were prepared in the same manner as the thus-obtained sample 401, except that the kind of yellow coupler and additives according to the present invention were changed as shown in Table 5. Each coupler was changed to another in an equimolar amount. In samples to which the compound according to the present invention was added, the amount of tricresylphosphate (an auxiliary solvent) was reduced in an amount corresponding to the amount (mass) of the compound added. After keeping these samples under conditions of 25 °C and 55%R.H. for 14 days, exposure was given so that a neutral gray density of 1.5 could be obtained uniformly over the area, followed by processing. After processing, the remaining rate (%) of density after irradiation to a 100,000-lux xenon light for 6 days was calculated, to evaluate the fastness property to light. The results are shown in Table 5.

Table 5

Sample No.	Yellow coupler	Compound of this invention		Fastness propertyto light (Density remaining rate (%))	Remarks
		Kind	Amount (mol% vs Cp)		
401	(45)	-	0	78	Comparative Example
402	(45)	TI-8	10	83	This invention
403	(45)	TI-24	10	85	This invention
404	(45)	TI-8 TI-24	10 10	87	This invention
405	(40)	-	0	76	Comparative Example
406	(40)	TI-8	10	81	This invention
407	(40)	TI-24	10	83	This invention
408	(40)	TI-8 TI-24	10 10	85	This invention

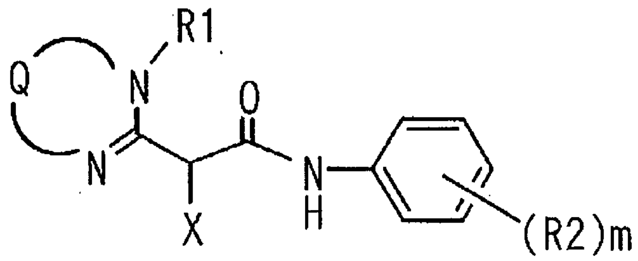
[0220] As is apparent from Table 5, the use of the compounds according to the present invention, in combination with the yellow couplers according to the present invention, siginificantly improved the fastness property to light.

[0221] Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

Claims

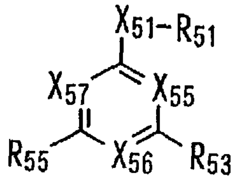
1. A silver halide color photographic light-sensitive material comprising at least one yellow dye-forming coupler represented by formula (I) shown below, and at least one compound selected from the group consisting of a metal complex and a compound represented by any one of the formulae (TS-I), (TS-II), (TS-III), (TS-IV), (TS-V), and (TS-VI) shown below, in at least one layer provided on a support:

formula (I)

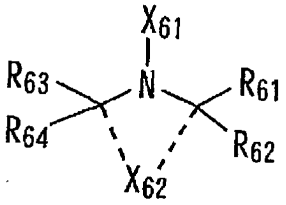


wherein, in formula (I), Q represents a group of non-metal atoms that form a 5- to 7-membered ring in combination with the -N=C-N(R1)-; R1 represents a substituent; R2 represents a substituent; m represents an integer of 0 to 5; when m is 2 or more, the multiple R2s may be the same or different, and the R2s may bond each other to form a ring; and X represents a hydrogen atom, or a group capable of being split-off upon a coupling reaction with an oxidized product of a developing agent;

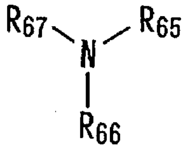
formula (TS-I)



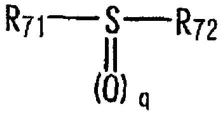
formula (TS-II)



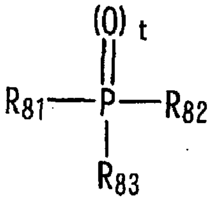
formula (TS-III)



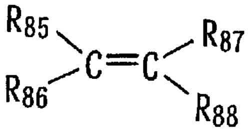
formula (TS-IV)



formula (TS-V)



formula (TS-VI)



wherein, in formula (TS-I), R_{51} represents a hydrogen atom, an aliphatic group, an aryl group, a heterocyclic group, an acyl group, an aliphatic oxycarbonyl group, an aryl oxycarbonyl group, an aliphatic sulfonyl group, an aryl sulfonyl group, a phosphoryl group, or -Si(R_{58})(R_{59})(R_{60}), in which R_{58}, R_{59}, and R_{60} each independently represent an aliphatic group, an aryl group, an aliphatic oxy group, or an aryloxy group; X_{51} represents -O-, or -N (R_{57})-, in which R_{57} has the same meaning as R_{51}; X_{55} represents -N=, or -C(R_{52})=; X_{56} represents -N=, or -C (R_{54})=; X_{57} represents -N=, or -C(R_{56})=; R_{52}, R_{53}, R_{54}, R_{55}, and R_{56} each independently represent a hydrogen atom, or a substituent; each combination of R_{51} and R_{52}, R_{57} and R_{56}, and R_{51} and R_{57} may combine together to form a 5- to 7-membered ring; each combination of R_{52} and R_{53}, and R_{53} and R_{54} may combine together to form a 5- to 7-membered ring, or a spiro ring, or a bicyclo ring; wherein the total number of carbon atoms of the compound represented by formula (TS-I) is 10 or more; and when, in formula (I), a 4-pyrimidone ring is formed by Q, and R1 is an alkyl group having 1 to 6 carbon atoms, any one of X_{55}, X_{56} and X_{57} is -N=; with the proviso that all of R_{51} to R_{57} simultaneously do not represent a hydrogen atom;

wherein, in formula (TS-II), R_{61}, R_{62}, R_{63}, and R_{64} each independently represent a hydrogen atom, or an aliphatic group; each combination of R_{61} and R_{62}, and R_{63} and R_{64} may combine together to form a 5- to 7-membered ring; X_{61} represents a hydrogen atom, an aliphatic group, an aliphatic oxy group, an aliphatic oxycarbonyl group, an aryl oxycarbonyl group, an acyl group, an acyloxy group, an aliphatic oxycarbonyloxy group, an aryl oxycarbonyloxy group, an aliphatic sulfonyl group, an aryl sulfonyl group, an aliphatic sulfinyl group, an aryl sulfinyl group, a sulfamoyl group, a carbamoly group, a hydroxy group, or an oxy radical group; X_{62} represents a group of non-metal atoms necessary to form a 5- to 7-membered ring; and when, in formula (I), Q forms a 4-pyrimidone ring and R1 is an alkyl group having 1 to 6 carbon atoms, X_{61} represents a hydrogen atom, an aliphatic group, an aliphatic oxy group, an aliphatic oxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, an aliphatic oxycarbonyloxy group, an aryl oxycarbonyloxy group, an aliphatic sulfonyl group, an aryl sulfonyl group, an aliphatic sulfinyl group, an aryl sulfinyl group, a sulfamoyl group, a carbamoly group, a hydroxyl group, or an oxy radical group;

wherein, in formula (TS-III), R_{65} and R_{66} each independently represent a hydrogen atom, an aliphatic group, an aryl group, an acyl group, an aliphatic oxycarbonyl group, an aryl oxycarbonyl group, a carbamoly group, an aliphatic sulfonyl group, or an aryl sulfonyl group; R_{67} represents a hydrogen atom, an aliphatic group, an aliphatic oxy group, an aryloxy group, an aliphatic thio group, an arylthio group, an acyloxy group, an aliphatic oxycarbonyloxy group, an aryl oxycarbonyloxy group, a substituted amino group, a heterocyclic group, or a hydroxyl group; each combination of R_{65} and R_{66}, and R_{66} and R_{67}, and R_{65} and R_{67} may combine together to form a 5-to 7-membered ring except 2,2,6,6-tetraalkylpyridine skeleton; wherein the total number of carbon atoms of R_{65} and R_{66} is 7 or more; with the proviso that R_{65} and R_{66} simultaneously do not represent a hydrogen atom;

wherein, in formula (TS-IV), R_{71} represents a hydrogen atom, an aliphatic group, an aryl group, a heterocyclic group, Li, Na, or K; R_{72} represents an aliphatic group, an aryl group, or a heterocyclic group; R_{71} and R_{72} may combine together to form a 5- to 7-membered ring; q represents 0, 1 or 2; wherein the total number of carbon atoms of R_{71} and R_{72} is 10 or more;

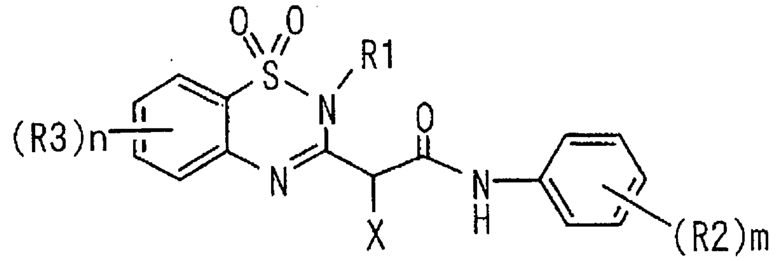
wherein, in formula (TS-V), R_{81}, R_{82}, and R_{83} each independently represent an aliphatic group, an aryl group, an aliphatic oxy group, an aryloxy group, an aliphatic amino group, or an aryl amino group; t represents 0 or 1; each combination of R_{81} and R_{82}, and R_{81} and R_{83} may combine together to form a 5- to 8-membered ring; wherein the total number of carbon atoms of R_{81}, R_{82}, and R_{83} is 10 or more; and

wherein, in formula (TS-VI), R_{85}, R_{86}, R_{87}, and R_{88} each independently represent a hydrogen atom, or a substituent, wherein any two of R_{85}, R_{86}, R_{87} and R_{88} may combine together to form a 5- to 7-membered ring except an aromatic ring only consisting of carbon atoms as a skeleton atom; and the total number of carbon atoms of the compound represented by formula (TS-VI) is 10 or more; with the proviso that all of R_{85}, R_{86}, R_{87}, and R_{88} simultaneously do not represent a hydrogen atom.

2. The silver halide color photographic light-sensitive material as claimed in claim 1, wherein Q in the formula (I) is a group represented by -C(-R11)=C(-R12)-SO_2- or -C(-R11)=C(-R12)-CO-, in which R11 and R12 are groups that bond with each other to form a 5- to 7-membered ring together with -C=C-, or they each independently represent a hydrogen atom or a substituent.

3. The silver halide color photographic light-sensitive material as claimed in claim 1 or 2, wherein the yellow dye-forming coupler represented by formula (I) is a yellow dye-forming coupler represented by formula (II):

formula (II)



wherein, R1 represents a substituent; R2 represents a substituent; m represents an integer of 0 to 5; when m is 2 or more, the multiple R2s may be the same or different, and the R2s may bond each other to form a ring; R3 represents a substituent; n represents an integer of 0 to 4; when n is 2 or more, the multiple R3s may be the same or different, and the R3s may bond each other to form a ring; and X represents a hydrogen atom, or a group capable of being split-off upon a coupling reaction with an oxidized product of a developing agent.

4. The silver halide color photographic light-sensitive material as claimed in claim 3, wherein, in the dye-forming coupler represented by the above-mentioned formula (II), R1 is a substituted or unsubstituted alkyl group.

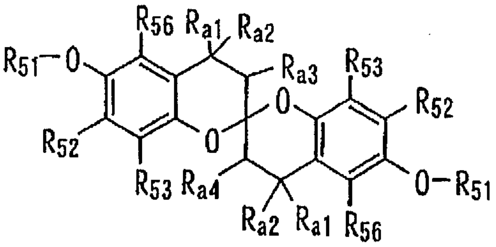
5. The silver halide color photographic light-sensitive material as claimed in claim 1, wherein the at least one yellow dye-forming coupler represented by formula (I) and the at least one compound selected from the group consisting of a metal complex and a compound represented by any one of formulae (TS-I), (TS-II), (TS-III), (TS-IV), (TS-V), and (TS-VI), are contained in the same layer.

6. The silver halide color photographic light-sensitive material as claimed in claim 1, wherein the dye-forming coupler represented by formula (I) is added in an amount 1 x 10^{-3} mole or more, per mol of silver halide.

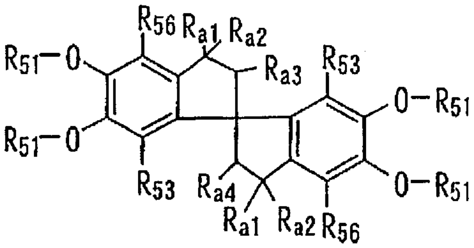
7. The silver halide color photographic light-sensitive material as claimed in claim 6, wherein the at least one compound selected from the group consisting of a metal complex and a compound represented by any one of formulae (TS-I), (TS-II), (TS-III), (TS-IV), (TS-V), and (TS-VI), is used in the rage of 1 to 400 mass%, based on the dye-forming coupler represented by formula (I).

8. The silver halide color photographic light-sensitive material as claimed in claim 1, wherein the compound represented by formula (TS-I) is a compound represented by any one of formulae (TS-IA), (TS-IB), (TS-IC), (TS-ID), (TS-IE), (TS-IF), (TS-IG), and (TS-IH);

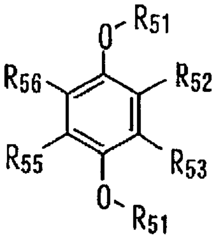
formula (TS-IA)



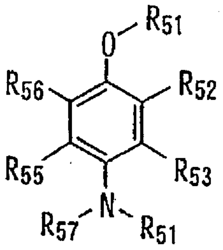
formula (TS-IB)



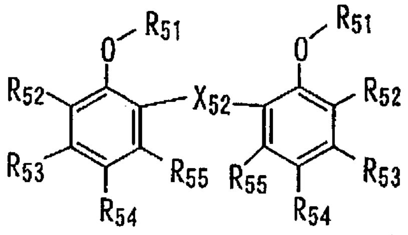
formula (TS-IC)



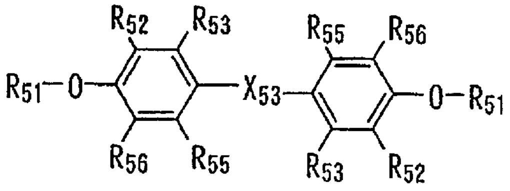
formula (TS-ID)



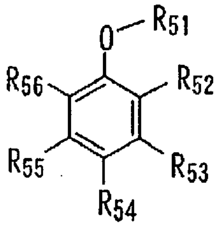
formula (TS-IE)



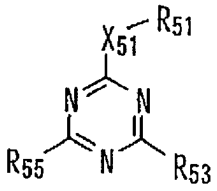
formula (TS-IF)



formula (TS-IG)



formula (TS-IH)



wherein, R_{51}, R_{52}, R_{53}, R_{54}, R_{55}, R_{56}, and R_{57} have the same meanings as those defined in formula (TS-I); R_{a1}, R_{a2}, R_{a3}, and R_{a4} each represent a hydrogen atom or an aliphatic group; and X_{52} and X_{53} each independently represent a divalent linking group.

9. The silver halide color photographic light-sensitive material as claimed in claim 8, wherein at least one compound represented by formula (TS-IB) is used in combination with at least one compound selected from the compounds represented by formula (TS-IE), (TS-IF), or (TS-IG).

10. The silver halide color photographic light-sensitive material as claimed in claim 1, wherein the at least one layer is an silver halide emulsion layer having silver chloride content of 95 mol% or more.

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EUROPEAN SEARCH REPORT

Application Number
EP 03 00 4333

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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