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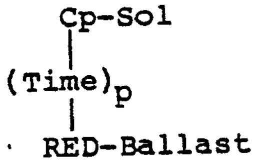
(71) Applicant: **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma Minami Ashigara-shi
Kanagawa 250-01(JP)

(72) Inventor: **Nakamura, Yoshisada**
c/o Fuji Photo Film Co., Ltd. No. 210, Nakanuma
Minami-Ashigara-shi Kanagawa(JP)
Inventor: **Ichijima, Seiji**
c/o Fuji Photo Film Co., Ltd. No. 210, Nakanuma
Minami-Ashigara-shi Kanagawa(JP)

(74) Representative: **Patentanwälte Grünecker, Kinkeldey, Stockmair & Partner**
Maximilianstrasse 58
D-8000 München 22(DE)

(54) Silver halide color photographic materials.

(57) A color photographic material comprising a support having provided thereon at least one blue, one green and one red light-sensitive silver halide emulsion layer and containing in one of said light-sensitive layers or a layer other than said light-sensitive layers a compound represented by formula (A)



$$\begin{array}{c}\mathrm{Cp\text{-}Sol}\\ |\\ (\mathrm{Time})_p\\ |\\ \mathrm{RED\text{-}Ballast}\end{array} \qquad (A)$$

wherein, Cp represents a group capable of releasing the $(\mathrm{Time})_p$-RED-Ballast group in a coupling reaction with the oxidized form of the developing agent; RED-ballast is a group which can reduce the oxidized form of the developing agent upon elimination from the Cp group; $(\mathrm{Time})_p$ represents a timing group; p is either zero or a positive integer; Sol is an alkali solubilizing group; and Ballast is a group which is resistant to diffusion.

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Silver halide color photographic materials

Field of the Invention

This invention concerns silver halide color photographic materials, and more particularly silver halide color photographic materials which are improved in respect of color staining and color fogging.

Background of the Invention

The method whereby color pictures are formed by exposing a silver halide color photographic material to light and subsequently processing the material in a color developing bath which contains a primary aromatic amine developing agent is well known.

When such a method is employed to form color pictures the above mentioned developing agent may undesirably be oxidized by the oxygen in the air and it is well known that the oxidized form of the developing agent reacts with the color couplers in the unexposed parts of the material or in the parts which have received a low level of exposure to form a dye so that color fogging occurs.

Furthermore, it is known that with the normal color sensitive materials which have two or more emulsion layers which have different color sensitivities and which contain color couplers which form different colors, the oxidized form of the developer which is formed on development in a layer of one color sensitivity diffuses into the layers which have other color sensitivities where it reacts with those couplers so that color staining (color mixing) occurs.

The use of hydroquinone based compounds has been suggested as a means of preventing the occurrence of undesirable color fogging and color staining.

For example, mono-n-alkylhydroquinones are disclosed in U.S. Patents 2,360,290, 2,419,613, 2,403,721 and 3,960,570, etc., mono-(branched alkyl)hydroquinones are disclosed in U.S. Patents 3,700,453 and 3,960,570, Japanese Patent Application (OPI) No. 156438/75 and in British Patent 1,363,921, etc., dialkyl substituted hydroquinones are disclosed in U.S. Patents 2,728,659, 2,732,300, 3,243,294 and 3,700,453, British Patents 752,146, 1,571,445, and 2,005,040, Japanese Patent Application (OPI) No. 156438/75 and Japanese Patent Publication No. 21249/75, etc. and arylhydroquinones have been disclosed in U.S. Patent 2,418,613.

These compounds certainly have some effect in the prevention of color fogging and color staining, but the effect is slight, and there is a further problem in that colored products continue to be formed even after these compounds have realized their inhibiting effects.

Thus hydroquinones substituted on the ring with electron attractive groups such as acyl groups, nitro groups, cyano groups, formyl groups, halogenated alkyl groups, etc., are suggested in U.S. Patent 4,198,239. These compounds are certainly better in respect of their ability to prevent the occurrence of color staining but there are problems in that they form colored products, their efficiency deteriorates during the manufacture and storage of the sensitive material and with the fact that they cause fogging of silver halide emulsions.

Furthermore, hydroquinones substituted with aliphatic acylamino groups, ureido groups, urethane groups, etc. have been suggested in U.S. Patent 4,198,239. These compounds are somewhat effective in preventing the occurrence of color staining and the developed images show only slight fog. However, the ability of these compounds to prevent color staining is still in need of improvement and there are problems with storage stability in that crystals are precipitated during the manufacture of the sensitive material.

Furthermore, hydroquinones which have been substituted with acylamino groups, aralkyl groups and alkyl groups which have sulfonic acid groups have been suggested in U.S. Patent 2,701,197, but these compounds diffuse during the manufacture and storage of the sensitive material into sensitive layers to which they have not been added, and this is disadvantageous not only in that it results in a deterioration of the anti-color staining and anti-color fogging effect in the layer to which the compounds have been added but also in that changes in the photographic performance of the other layers occur during the manufacture and storage of the sensitive material.

Furthermore, hydroquinones substituted with sulfonamido groups are disclosed in U.S. Patent 4,584,264 but these compounds still do not have the ability to prevent the occurrence of color staining satisfactorily.

Furthermore, hydroquinones which have electron attractive groups, for example, hydroquinones which have been substituted with carbamoyl groups, are disclosed in Japanese Patent Application (OPI) No.

22237/82 but these compounds are readily oxidized during the manufacture and storage of the sensitive material and there are problems with changes in photographic performance and with the marked coloration of the oxidized forms.

Furthermore, compounds which have a hydroquinone residual group and a coupler residual group in the same molecule are disclosed in Japanese Patent Publication No. 7578/80. However, these are very different from the compounds of the present invention, forming a colored image by way of a coupling reaction in the course of the development process, and by their nature they are incompatible with the prevention of color staining and color fogging which is the aim of the present invention.

Furthermore, pyrogallol derivatives are suggested as anti-color staining agents in U. S. Patent 4,474,874. These have a marked inhibiting effect on color staining but they diffuse into layers to which they have not been added during the manufacture and storage of the sensitive material and this is disadvantageous in that it causes changes to occur the photographic performance of the other layers.

Furthermore, the use of compounds which resemble the compounds of this invention are in Japanese Patent Application (OPI) Nos. 84646/86 and 102646/86 but these compounds react with the oxidized form of the developing agent and are used for form dyes which are fast to diffusion during development and they are essentially different from this present invention.

Moreover, compounds which undergo a coupling reaction with the oxidized form of a color developing agent and which can form wash-out type coupling products have been disclosed in Japanese Patent Application (OPI) No. 20037/86. These compounds do have the ability to prevent color staining and color fogging. However the compounds are essentially different from the compounds of this present invention, having the capacity to deactivate only the amount of the oxidized form of the developing agent which is needed in the coupling reaction, their capacity is not greatly different from that of the conventional anti-color staining agents and they cannot be said to have a satisfactory capacity for preventing the occurrence of color staining and color fogging.

A first object of the invention is to provide photosensitive materials which give rise to little color staining and color fogging.

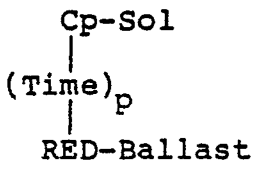
A second object of the invention is to provide photosensitive materials which contain anti-color staining agents which are not liable to form colored products during storage or development.

A third object of the invention is to provide photosensitive materials which have excellent color reproduction properties and which have a photographic performance which is stable over long period of time with no change in the anti-color staining and anti-color fogging during manufacture and/or storage.

A fourth object of the invention is to provide photosensitive materials which have thin emulsion layers and intermediate layers.

SUMMARY OF THE INVENTION

These and other objects are attained and the problems referred to above are overcome by means of color photographic material wherein anti-color staining, anti-color fogging compounds which are represented by the general formula (A)



$$\begin{array}{c}\text{Cp-Sol}\\ |\\ (\text{Time})_p\\ |\\ \text{RED-Ballast}\end{array} \qquad \text{(A)}$$

wherein, Cp represents a group which can release the $(\text{Time})_p$-RED-Ballast group in a coupling reaction with the oxidized form of the developing agent; RED-Ballast is a group which is released from Cp group either immediately, or via the $(\text{Time})_p$ group and which is capable of reducing the oxidized form of the developing agent; $(\text{Time})_p$ represents a timing group and p is either 0 or a positive integer; Sol is a group to diffuse a coupling product from a photographic layer, and Ballast is a group which renders the compound resistant to diffusion, are included in photographic materials preferably in layers other than the photosensitive silver halide emulsion layers thus color photographic material having at least one blue, one green and one red sensitive silver halide emulsion layer formed on a support.

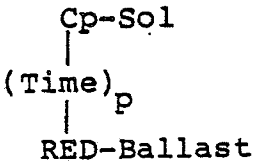
DETAILED DESCRIPTION OF THE INVENTION

The distinguishing features of the compounds of this invention which are represented by the general formula (A) are that in the state in which the RED group is bonded to the Cp residual group, there is no reduction capacity or only a very weak reduction capacity, and that the ability of the RED group to reduce the oxidized form of the developing agent is initiated by its elimination from the Cp residual group. Thus, when the compound (A) is used, a first molecule of the oxidized form of the developing agent is consumed for releasing the RED group from the Cp residual group and a second molecule is consumed by the reduction due to the RED group and so more of the oxidized form of the developing agent is consumed by one molecule of these compounds than is the case with the compounds which reduce the oxidized form of the developer which have been used in the past (for example the compounds disclosed in the prior patents mentioned above).

In the case of processing operations which involve the execution of a development process prior to color development, the capacity of the compound of this invention is not diminished in the initial development process and it is still able to realize its function during the color development process.

The compound (A) of the invention are described in detail below.

General formula (A)

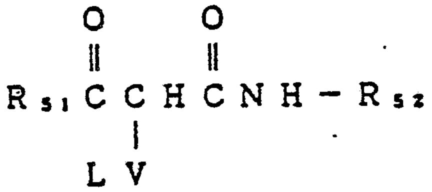


$$\begin{array}{l} \mathrm{Cp\text{-}Sol} \\ \quad | \\ \mathrm{(Time)}_p \\ \quad | \\ \mathrm{RED\text{-}Ballast} \end{array} \qquad \mathrm{(A)}$$

In general formula (A), Cp may be any group capable of releasing the RED-Ballast group in a coupling reaction with the oxidized form of a developing agent.

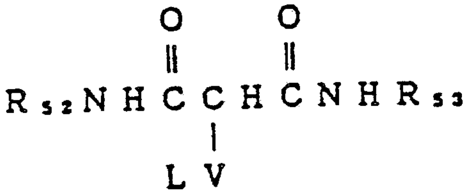
Preferred Cp groups are represented by the general formulae (Cp-1), (Cp-2), (Cp-3), (Cp-4), (Cp-5), (Cp-6), (Cp-7) or (Cp-8) which are shown below.

General formula (Cp-1)



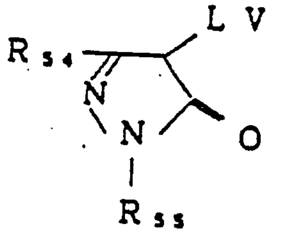
$$R_{51}\overset{\displaystyle O}{\overset{\|}{C}}\underset{\displaystyle LV}{\underset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}NH-R_{52} \qquad \mathrm{(Cp\text{-}1)}$$

General formula (Cp-2)



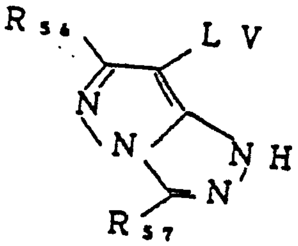
$$R_{52}NH\overset{\displaystyle O}{\overset{\|}{C}}\underset{\displaystyle LV}{\underset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}NHR_{53} \qquad \mathrm{(Cp\text{-}2)}$$

General formula (Cp-3)



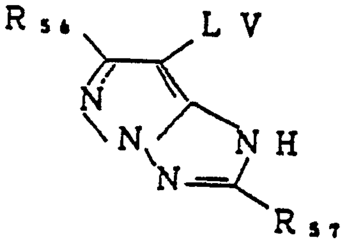
(Cp-3)

General formula (Cp-4)



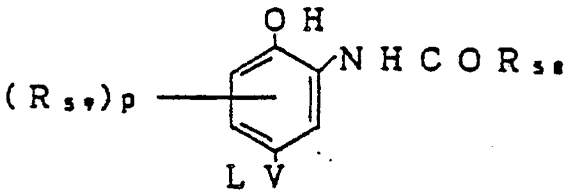
(Cp-4)

General formula (Cp-5)



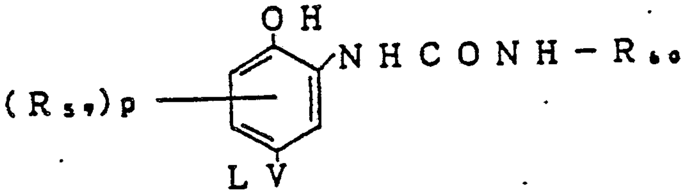
(Cp-5)

General formula (Cp-6)



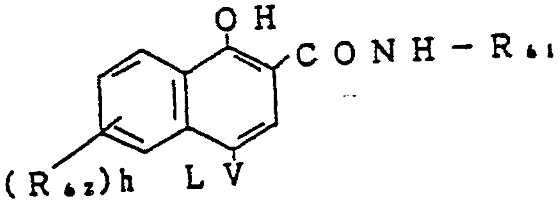
(Cp-6)

General formula (Cp-7)



(Cp-7)

General formula (Cp-8)

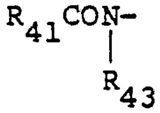
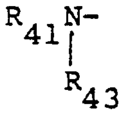
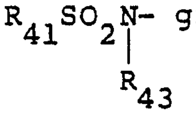
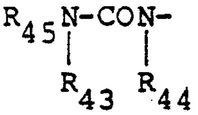


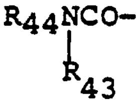
(Cp-8)

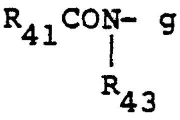
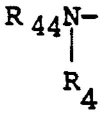
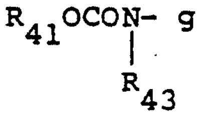
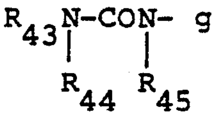
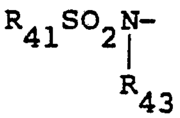
The significance of the groups R_{51} to R_{62}, LV, p and h is described below.

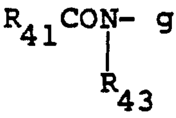
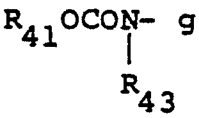
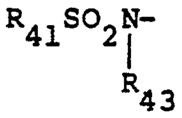
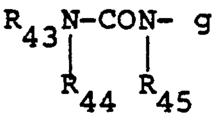
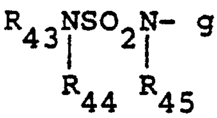
In these formulae, R_{51}, R_{52}, R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{59}, R_{60}, R_{61}, and R_{62}, which may be the same or different, preferably have not more than a total of 15 carbon atoms. Furthermore, in general formula (Cp-1), at least one of R_{51} and R_{52} represents a linking group with the Sol group or the Sol group itself. Similarly in general formula (Cp-2) at least one of R_{52} and R_{53}, in general formula (Cp-3) at least one of R_{54} and R_{55} in general formula (Cp-4) at least one of R_{56} and R_{57}, in general formula (Cp-5) at least one of R_{56} and R_{57}, in general formula (Cp-6) at least one of R_{58} and R_{59}, in general formula (Cp-7) at least one of R_{59} and R_{60} and in general formula (Cp-8) at least one of R_{61} and R_{62} is, like R_{51} or R_{52} in general formula (Cp-1), a linking group with the Sol group or the Sol group itself.

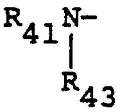
In the description below R_{41} represents an aliphatic group, aromatic group or heterocyclic group, R_{42} represents an aromatic group or a heterocyclic group and R_{43}, R_{44} and R_{45} represent hydrogen atoms, aliphatic groups, aromatic groups or heterocyclic groups.

R_{51} has the same significance as R_{41}. R_{52} and R_{53} both have the same significance as R_{42}. R_{54} represents a group which has the same significance as R_{41}, an  $R_{41}CO\underset{R_{43}}{\underset{|}{N}}-$ group, an  $R_{41}\underset{R_{43}}{\underset{|}{N}}-$ group, an  $R_{41}SO_2\underset{R_{43}}{\underset{|}{N}}-$ group, an $R_{41}S-$ group, an $R_{43}O-$ group, an  $R_{45}\underset{R_{43}}{\underset{|}{N}}-CO\underset{R_{44}}{\underset{|}{N}}-$ group, an $R_{43}OOC$-group, an


$R_{44}\underset{R_{43}}{\underset{|}{N}}CO-$

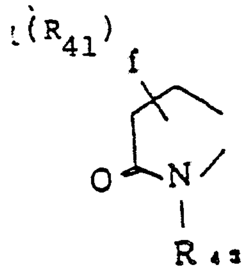
group or an N≡C-group. R_{55} represents a group which has the same significance as R_{41}. R_{56} and R_{57} each represents groups which have the same significance as the R_{43} group, $R_{41}S$-groups, $R_{43}O$-groups,  $R_{41}CO\underset{R_{43}}{\underset{|}{N}}-$ groups,  $R_{44}\underset{R_{43}}{\underset{|}{N}}-$ groups,  $R_{41}OCO\underset{R_{43}}{\underset{|}{N}}-$ groups,  $R_{43}\underset{R_{44}}{\underset{|}{N}}-CO\underset{R_{45}}{\underset{|}{N}}-$ groups or  $R_{41}SO_2\underset{R_{43}}{\underset{|}{N}}-$ groups. R_{58} represents a group which has the same significance as R_{41}.

In formula (Cp-7), R_{59} is a group which has the same significance as R_{41}, an  $R_{41}CO\underset{R_{43}}{\underset{|}{N}}-$ group, an  $R_{41}OCO\underset{R_{43}}{\underset{|}{N}}-$ group, an  $R_{41}SO_2\underset{R_{43}}{\underset{|}{N}}-$ group, an  $R_{43}\underset{R_{44}}{\underset{|}{N}}-CO\underset{R_{45}}{\underset{|}{N}}-$ group, an  $R_{43}\underset{R_{44}}{\underset{|}{N}}SO_2\underset{R_{45}}{\underset{|}{N}}-$ group, an $R_{41}O$-group, an $R_{41}S$-group, a halogen atom or an

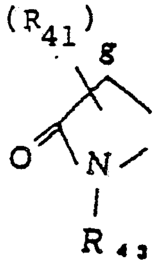

$R_{41}\underset{R_{43}}{\underset{|}{N}}-$

group.

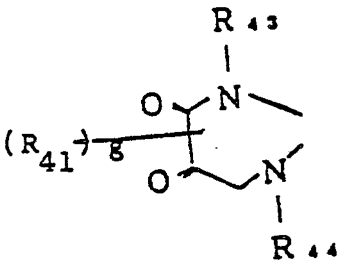
Moreover, p is a number of value 0 to 3. When p is 2 or more, the plurality of R_{59} groups may be the same or different substituent groups. Furthermore, the R_{59} groups may be divalent groups which are joined to form a ring structure. Examples of divalent groups for the formation of ring structures are indicated below.



group,



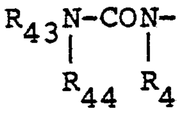
group or a



group.

Here f represents an integer of value 0 to 4 and g represents an integer of value 0 to 2. R_{60} represents a group which has the same significance as R_{41}.

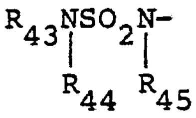
In formula (Cp-8), R_{61} represents a group which has the same significance as R_{41}. R_{62} represents a group which has the same significance as R_{41}, an R_{41}CONH-group, and R_{41}OCONH-group, an $R_{41}SO_2$NH-group, an



$$\underset{R_{44}}{R_{43}N}-CO\underset{R_{45}}{N}-$$

group,

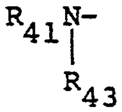
an



$$\underset{R_{44}}{R_{43}N}SO_2\underset{R_{45}}{N}-$$

group, an

R_{43}O-group, an R_{41}S-group, a halogen atom or an



$$R_{41}\underset{R_{43}}{N}-$$

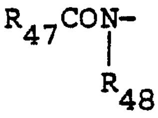
group. Moreover, h represents an integer of value 0 to 4. In cases where there is a plurality of R_{62} groups these groups may be the same or different.

The aliphatic groups mentioned above are saturated or unsaturated, chain or ring like, linear chain or branched chain, substituted or unsubstituted aliphatic groups which have from 1 to 20, and preferably from 1 to 10, carbon atoms. Typical examples are a methyl group, an ethyl group, a propyl group, an iso-propyl group, a butyl group, a tert-butyl group, an iso-butyl group, a tert-amyl group, a hexyl group, a cyclohexyl group, a 2-ethylhexyl group, an octyl group, a 1,1,3,3-tetramethylbutyl group, and a decyl group.

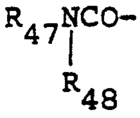
The aromatic groups have from 6 to 10 carbon atoms and are preferably substituted or unsubstituted phenyl groups.

The heterocyclic groups are preferably 3-to 8-membered substituted or unsubstituted heterocyclic groups which have atoms selected from among nitrogen, oxygen and sulfur atoms as the hetero atoms and which may have from 1 to 12, and preferably from 1 to 8, carbon atoms. Typical examples of heterocyclic groups include a 2-pyridyl group, a 4-pyridyl group, a 2-thienyl group, a 2-furyl group, a 2-imidazolyl group, a pyrazinyl group, a 2-pyrimidinyl group, a 1-imidazolyl group, a 1-indolyl group, a phthalimido group, a 1,3,4-thiadiazol-2-yl group, a benzoxazol-2-yl group, a 2-quinolyl group, a 2,4-dioxo-1,3-imidazolidin-5-yl group, a 2,4-dioxo-1,3-imidazolidin-3-yl group, a succinimido group, a 1,2,4-triazol-2-yl group and a 1-pyrazolyl group.

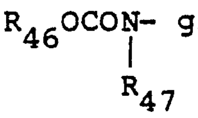
Typical substituents in cases where the aforementioned aliphatic groups, aromatic groups and heterocyclic groups have substituents include halogen atoms, $R_{47}O$-group, $R_{46}S$-group,



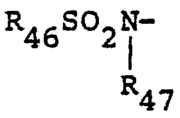
$R_{47}CO\underset{R_{48}}{\underset{|}{N}}-$ group,



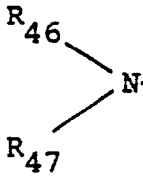
$R_{47}\underset{R_{48}}{\underset{|}{N}}CO-$ groups,



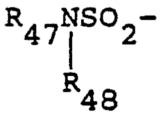
$R_{46}OCO\underset{R_{47}}{\underset{|}{N}}-$ groups,



$R_{46}SO_2\underset{R_{47}}{\underset{|}{N}}-$ groups,

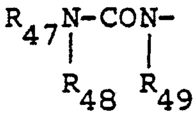


$(R_{46})(R_{47})N-$ groups,

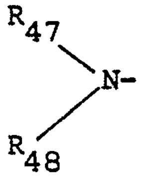


$R_{47}\underset{R_{48}}{\underset{|}{N}}SO_2-$ groups,

$R_{46}SO_2$-groups, $R_{47}OCO$-groups,

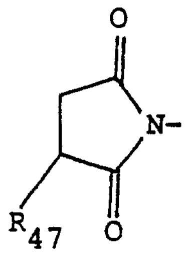


$R_{47}\underset{R_{48}}{\underset{|}{N}}-CO\underset{R_{49}}{\underset{|}{N}}-$ groups,



$(R_{47})(R_{48})N-$

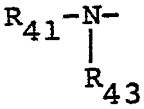
group, groups which have the same significance as R_{46},



groups, $R_{46}COO$-groups, $R_{47}OSO_2$-groups, cyano groups and nitro groups. Here, R_{46} represents an aliphatic group, an aromatic group or a heterocyclic group and R_{47}, R_{48} and R_{49} each represents aliphatic groups, aromatic groups, heterocyclic groups or hydrogen atoms. The significance of the terms aliphatic group, aromatic group and heterocyclic group as used here is the same as that defined above.

The preferred substituents represented by R_{51} to R_{62}, p and h are described below.

R_{51} is preferably an aliphatic group or an aromatic group. R_{52}, R_{53} and R_{55} are preferably aromatic groups. R_{54} is preferably an $R_{41}CONH$-group or an



$$R_{41}-\underset{\displaystyle R_{43}}{\underset{|}{N}}-$$

group. R_{56} and R_{57} are preferably aliphatic groups or aromatic groups, R_{41}O-groups or R_{41}S-groups. R_{58} is preferably an aliphatic group or an aromatic group. R_{59} in general formula (Cp-6) is preferably a chlorine atom, an aliphatic group or an $_{41}$CONH-group. Moreover, p preferably is an integer of from 0 to 2. R_{60} is preferably an aromatic group. R_{59} in general formula (Cp-7) is preferably an R_{41}CONH-group. Moreover, p in general formula (Cp-7) is preferably from 0 to 2. R_{61} is preferably an aliphatic group or an aromatic group. In general formula (Cp-8), the value of h is preferably 0 or 1. R_{62} is preferably an R_{41}OCONH-group, an R_{41}CONH-group or an $R_{41}SO_2$NH-group and the preferred substitution position of these groups is the 5-position of the naphthol ring.

Typical examples other than a linking group with the Sol group or the Sol group itself comprised of R_{51} to R_{62} are described below.

R_{51} may be a tert-butyl group, a 4-methoxyphenyl group, a 2-furyl group, a phenyl group, a methyl group, a 2-chlorophenyl group or an acetoamidophenyl group. R_{52} and R_{53} may be 2-chloro-5-methoxycarbonylphenyl groups, 2-chloro-5-ethoxycarbonylphenyl groups, 2-chloroisopropoxycarbonylphenyl groups, 2-chloroacetoamidophenyl groups, 2-chloropropionamidophenyl groups, 2-methoxyphenyl groups, 2-methoxy-5-methoxycarbonylphenyl groups, 2-methoxy-5-ethoxycarbonylphenyl groups, 2-pyridyl groups, phenyl groups, 2-chloro-5-methanesulfonamido groups, 2,4-dichlorophenyl groups, 2-chloro-5-methoxycarbonylethoxycarbonylphenyl groups, 2-chlorophenyl groups, or 2-butyloxyphenyl groups. R_{54} may be a 3-acetoamidobenzamido group, a 5-phenoxyacetamidoanilino group, a 5-phenoxyacetamidobenzamido group, a 2-chloro-5-methylsuccinimidoanilino group, a 2,2-dimethylpropanimido group, a butanamido group, a pyrrolidino group, or an N,N-dimethylamino group.

R_{55} may be a 2,4,6-trichlorophenyl group, a 2-chlorophenyl group, a 2,5-dichlorophenyl group, a 2,3-dichlorophenyl group, a 2,6-dichloro-4-methoxyphenyl group, or a 2,6-dichloro-4-methanesulfonylphenyl group.

R_{56} may be a methyl group, an ethyl group, an isopropyl group, a methoxy group, an ethoxy group, a methylthio group, an ethylthio group, a 3-phenylureido group, a 3-meth ylureido group, a 2-phenoxyethoxy group, a 2-methoxyphenoxy group, or 2,4-dimethoxyphenoxy-group.

R_{57} may be a 3-phenoxypropyl group, a 3-(2-methoxyethoxyphenyl)propyl group, a methoxy group, an ethoxy group, a methylthio group, an ethylthio group, a methyl group, an ethyl group, a propyl group, an iso-propyl group, a tert-butyl group, a 1-methyl-2-(2-ethoxy-5-methylphenylsulfonamido)ethyl group, a 1-methyl-2-(2-methoxyethoxyphenylsulfonamido)ethyl group, a 1,1-dimethyl-2-phenylsulfonamidoethyl group, a 3-methanesulfonamidophenyl group, a 3,5-dichlorophenyl group, a 3-nitrophenyl group, an ethylthio group or a phenylthio group.

R_{58} may be a 2-chlorophenyl group, a pentafluorophenyl group, a pentafluoropropyl group, a butyl group, a propyl group, an ethyl group, a methyl group or a furyl group.

R_{59} may be a chlorine atom, a fluorine atom, a methyl group, an ethyl group, a propyl group, a butyl group, an iso-propyl group or a 2-phenoxyacetamido group.

R_{60} may be a 4-cyanophenyl group, a 2-cyanophenyl group, a 4-methanesulfonylphenyl group, a 4-ethanesulfonylphenyl group, a 4-ethoxycarbonylphenyl group, a 4-N,N-diethylsulfamoylphenyl group, a 3,4-dichlorophenyl group, or a 3-methoxycarbonylphenyl group.

R_{61} may be a butyl group, a 3-phenoxypropyl group, a 3-phenoxybutyl group, a 3-ethoxypropyl group, a 3-methoxy propyl group, a 2-methoxyphenyl group, a tert-butyl group, a 2,5-dimethoxyphenyl group, or a 2,5-dichlorophenyl group.

R_{62} may be an isobutyloxycarbonylamino group, an ethoxycarbonylamino group, a phenylsulfonylamino group, a methanesulfonamido group, a butanesulfonamido group, a 4-methylbenzenesulfonamido group, a benzamido group, a trifluoroacetamido group, a 3-phenylureido group, a butoxycarbonylamino group or an acetamido group.

When R_{51} to R_{62} each represents Sol group itself, Sol group represents an alkali solubilizing group. Preferable alkali solubilizing group includes a hydroxy group, a carboxylic acid group or salts thereof, a sulfinic acid group or salts thereof, a sulfonic acid group or salts thereof, an amino group, a phosphinic acid group, a phosphonic acid group or salts thereof, etc. In cases where Sol group represents a salt, this may be, for example, a sodium salt, a potassium salt or an ammonium salt. Most preferable Sol group is a carboxylic acid group.

When R_{51} to R_{62} each represents a linking group with a Sol group, R_{51} to R_{62} each represents a group wherein one or two hydrogen atoms in the preferable group represented by R_{51} to R_{62} link to the above described water solubilizing group. Representative groups represented by R_{51} to R_{62} are illustrated below.

R_{51} may be a 3-carboxyphenyl group, a 2-hydroxyphenyl group, a 4-hydroxyphenyl group, a 3,5-dicarboxyphenyl group, a 2-hydroxy-2-methylbutyl group, a 3-carboxypropyl group or a 2-hydroxyethyl group.

R_{52} and R_{53} each may be a 2-chloro-4-hydroxyphenyl group, a 2-chloro-5-carboxyphenyl group, a 3,5-dicarboxyphenyl group, a 4-carboxyphenyl group, a 4-sulfophenyl group or a 3-(3-carboxy)propioneamido group.

R_{54} may be a 3-carboxypropioneamido group, a hydroxymethyl group, a carboxymethyl group, a carboxyethyl group or a sulfomethyl group.

R_{55} may be a 4-(3-carboxy)propioneamidophenyl group, a 4-hydroxyphenyl group, a 3-carboxyphenyl group, a 3,5-dicarboxyphenyl group or a 2-hydroxyethyl group.

R_{56} may be a 2-hydroxyethyloxy group, a 2-carboxyethyloxy group, a carboxymethyloxy group, a 2-hydroxyphenoxy group, a 4-hydroxyphenoxy group or a 2,4-dihydroxyphenoxy group.

R_{57} may be a 2-carbamoylethyl group, a 1-methyl-2-carbamoylethyl group, a 2-sulfamoylethyl group, a 1-methylsulfoamoylethyl group, a 1-methyl-2-carboxyethyl group, a 2-(3-carboxypropioneamido)ethyl group, a carboxymethylthio group, a 3-carboxyphenyl gorup, a 3,5-dicarboxyphenyl group or a 4-hydroxyphenyl group.

R_{58} may be a 4-carboxyphenyl group, a 3-carboxyphenyl group, a 4-sulfophenyl group, a 2-carboxyethyl group, a 3,5-dicarboxyphenyl group, a 2,5-dihydroxyphenyl group, a 3-(3-carboxypropioneamido)-phenyl group, a carboxymethyl group or a 3-hydroxypropioneamido group.

R_{59} may be a 3-carboxypropioneamido group, a carboxy group, a hydroxy group, a sulfo group, a 2-carboxyethyloxy group, a carboxymethylthio group or a 3-hydroxypropioneamido group.

R_{60} and R_{61} each may be the same group as R_{58}.

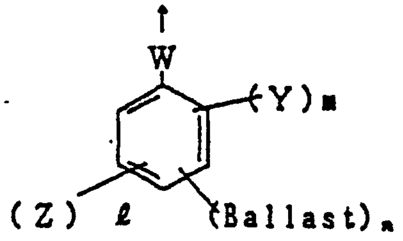
R_{62} may be the same group as R_{59}, a carboxymethoxycarbonylamino group, a hydroxymethoxycarbonylamino group or a carboxymethoxysulfamoyl group.

LV represents the $(Time)_p$-RED-Ballast group in the general formula (A). RED-Ballast group represents a group which is releasable from Cp group and is capable of reducing the oxidized form of the developing agent.

In general, all of those compounds which obey the Kendall-Pelz law are included as having a reduction capacity (for more details, see The Theory of the Photographic Process, Vol. 4 by T.H. James, pages 298-300, published by Macmillan, 1976).

The preferred RED-Ballast groups in general formula (A) can be represented by the general formulae (B), (C) and (D) below.

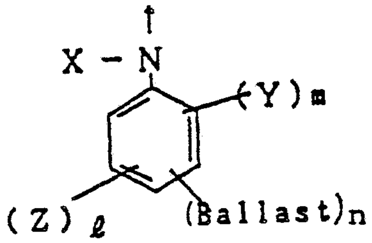
General formula (B)



(B)

In general formula (B), the arrow indicates the linking position with the Cp group and W represents an oxygen atom or a sulfur atom. Furthermore, Z represents an -OH group, $-OCOR^1$ group, $-OSOR^1$ group, $-OSO_2R^1$ group, $-NHR^1$ group, $-NR^2SOR^1$ group and/or an $-NR^2SO_2R^1$ group located in positions ortho and/or para to the linking group W. Here, R^1 represents an aliphatic group, an aromatic group or a heterocyclic group, R^2 represents a hydrogen atom or an aliphatic group and ℓ is an integer of value from 1 to 3. Y represents a substituent on the benzene ring as defined below and m is an integer of value from 0 to 3. Ballast represents a group which is fast to diffusion and n is an integer of value 1 or 2. However, the sum total of ℓ, m and n is not greater than 5.

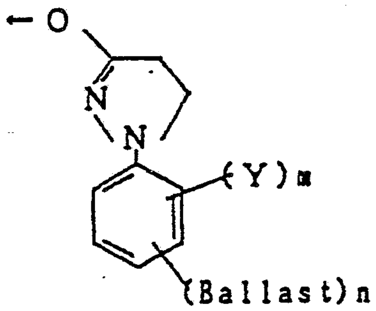
General Formula (C)



(C)

In general formula (C), an arrow indicates the linking position with the Cp group. X represents an electron attractive group, such as acyl groups e.g., an acetyl group, a benzoyl group, etc., alkylsulfonyl groups, e.g., a methylsulfonyl group, -, etc., arylsulfonyl group, e.g., a p-toluenesulfonyl group, a p-bromobenzenesulfonyl group, etc. Furthermore, the groups represented by Z are substitued in a position ortho and/or para to the nitrogen atom and moreover Z, R^1, R^2, Y, the Ballast group and, m and n habe the same significane as in general formula (B).

General Formula (D)



(D)

In general formula (D), the arrow and Y have the same significance as in general formula (B), m is an integer of value 0 to 4 and n is an integer of value 1 to 2. However, the sum total of m and n is not more than 5.

When p is greater than or equal to 1 in general formula (A), the timing group which is represented by $(\text{Time})_p$is a divalent or trivalent organic group which bonds the -RED-Ballast part to the coupling part of Cp. These two parts are bonded together directly when p is zero.

The mechanism by which the -RED-Ballast group is released when the $(\text{Time})_p$ group is present can be, for example, that which is seen with a photographically useful group (referred to below as a PUG) releasing timing type coupler.

This may involve, for example, the methods in which a PUG is released by means of a post elimination intramolecular nucleophilic substitution reaction as disclosed in U.S. Patent 4,248,962, the methods in which a PUG is released by means of a post elimination electron transfer along a conjugated system as disclosed in U.S. Patent 4,409,323 and Japanese Patent Application (OPI) Nos. 154234/82 (Research Disclosure No. 21228) and 188035/82, the methods in which a PUG is released as a result of a post elimination intramolecular nucleophilic substitution reaction occurring by means of a nucleophilic group which is newly formed by an electron transfer along a conjugated system as disclosed in Japanese Patent Application (OPI) Nos. 56837/82 and 209740/83, or the methods in which a PUG is released by the post elimination cleavage of a hemiacetal as disclosed in Japanese Patent Application Nos. 75475/84 and 89719/84.

Any group which is substantially fast to diffuse in a layer containing the compounds of the present invention may used as the Ballast group. The Ballast group is preferably an organic group having 8 or more of carbon atoms and more preferably 16 or more of carbon atoms.

The compounds of general formula (A) of this invention may form dimers, trimers or polymers at the Ballast position.

The aliphatic groups, aromatic groups and heterocyclic groups in general formulae (A) to (D) and in this specification are defined below.

Thus the aliphatic group, aromatic group and heterocyclic group substituent groups and Y and the substituent groups in the general formulae (A) to (D) are halogen atoms, hydroxyl groups, nitro groups, cyano groups, aliphatic groups, aromatic groups, heterocyclic groups, aliphatic oxy groups, aromatic oxy groups, aliphatic thio groups, aromatic thio groups, unsubstituted or substituted amino groups, carbonyl groups, sulfonyl groups, sulfoxide groups, aliphatic oxycarbonyl groups, aromatic oxycarbonyl groups, aliphatic oxysulfonyl groups, aromatic oxysulfonyl groups, carbamoyl groups, sulfamoyl groups, acyloxy groups, acylamino groups, sulfonamido groups, ureido groups, sulfamoylamino groups, aliphatic oxycarbonylamino groups, etc. However, Y is a photographically useful group.

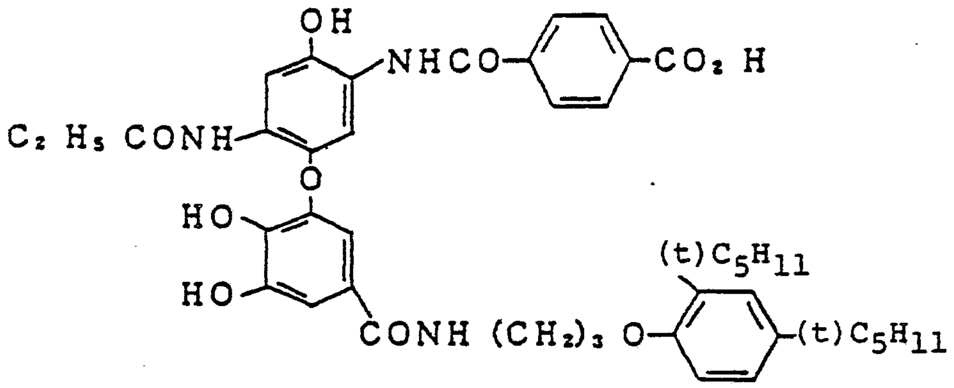
The compounds of this invention can be included in the layers of sensitive material, for example, in the photosensitive emulsion layers (blue sensitive layers, green sensitive layers and red sensitive layers) or in the layers adjacent to these layers (for example, in the intermediate layers which are adjacent to different color sensitive emulsion layers and intermediate layers between color sensitive emulsion layers which are essentially the same), the protective layers and anti-halation agents containing layers, etc. but they are preferably included in the intermediate layers between emulsion layers which have different color sensitivities.

The compounds of this invention may be used conjointly with conventional anti-color mixing agents such as the hydroquinones, catechols, gallic acids, etc.

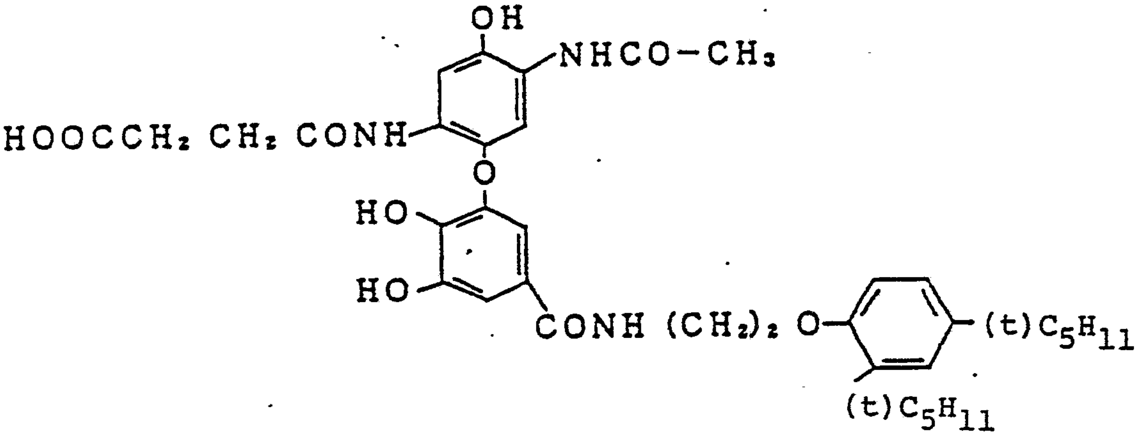
When the compounds of this invention are included in intermediate layers, anti-halation layers and protective layers the amount added is from 1×10^{-7} to 1×10^{-2} mol per square meter, preferably from 10^{-6} to 3×10^{-3} mol per square meter and most desirably from 1×10^{-5} to 1×10^{-3} mol per square meter. When the compounds are added to a silver halide emulsion layer the amount is from 1×10^{-4} to 1 mol, preferably from 3×10^{-4} to 3×10^{-1} mol, and most desirably from 1×10^{-3} to 1×10^{-1} mol, per mol of silver contained in the layer.

Actual examples of compounds which are included in this invention are indicated below but the invention is not limited to these compounds.

A-1


OH
NHCO
CO₂ H
C₂ H₅ CONH
O
HO
HO
(t)C5H11
CONH (CH₂)₃ O
(t)C5H11

A-2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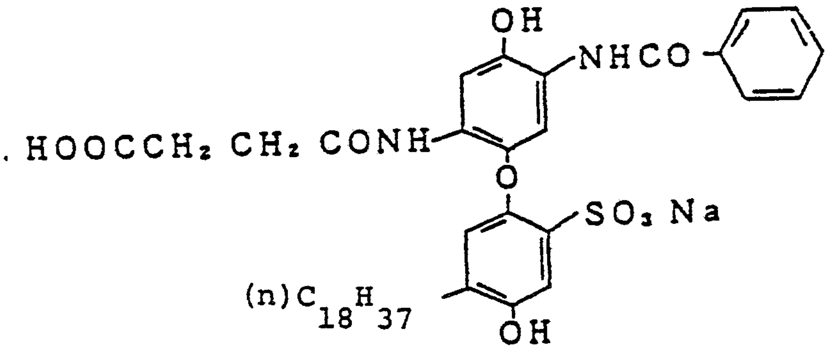
NHCO-CH₃
HOOCCH₂ CH₂ CONH
O
HO
HO
CONH (CH₂)₂ O
(t)C5H11
(t)C5H11

A-3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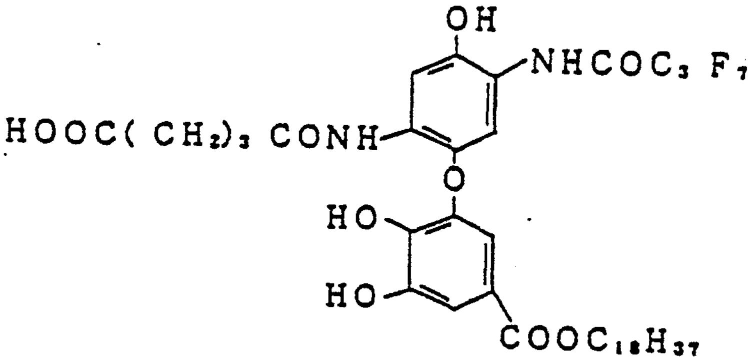
NHCO
HOOCCH₂ CH₂ CONH
O
SO₃ Na
(n)C18H37
OH

A-4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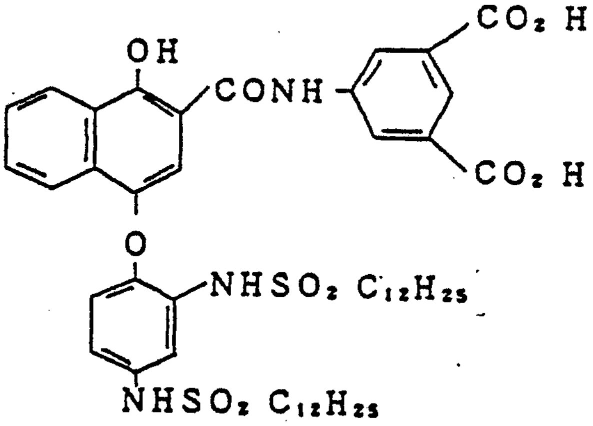
NHCOC₃F₇
HOOC(CH₂)₃CONH
O
HO
HO
COOC₁₈H₃₇

A-5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CONH
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CO₂H
O
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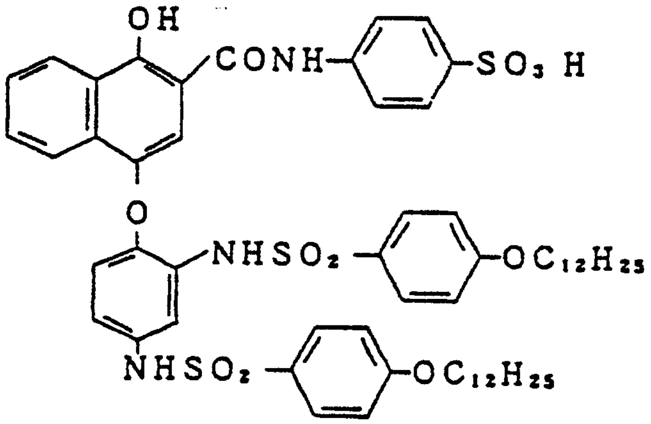
NHSO₂C₁₂H₂₅

A-6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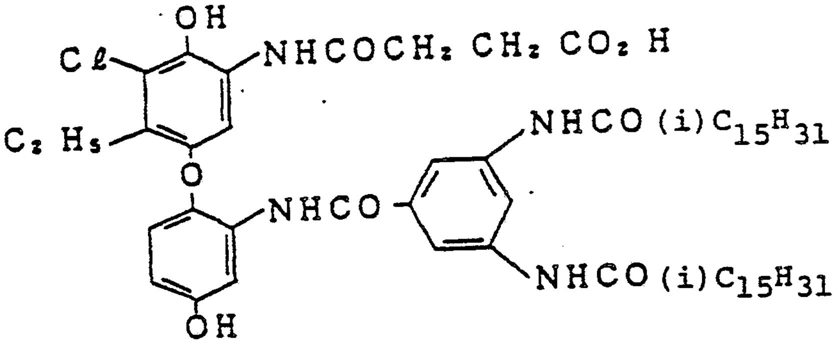
CONH
SO₃H
O
NHSO₂
OC₁₂H₂₅
NHSO₂
OC₁₂H₂₅

A-7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Cℓ
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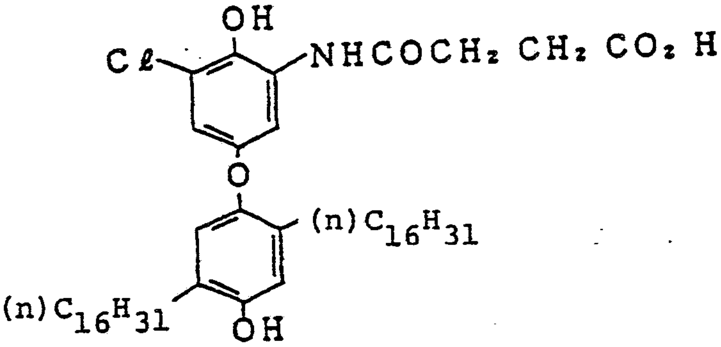
C₂ H₅
O
NHCO
NHCO (i)C15H31
NHCO (i)C15H31
OH

A-8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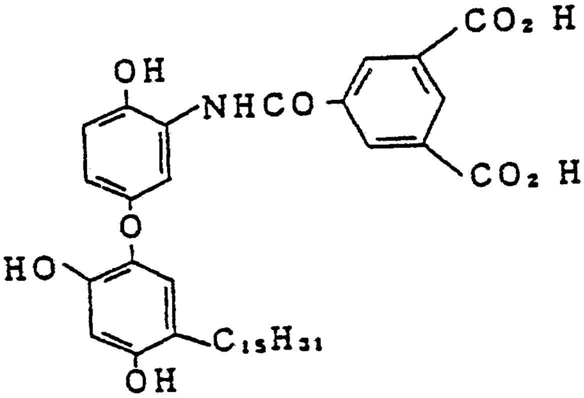
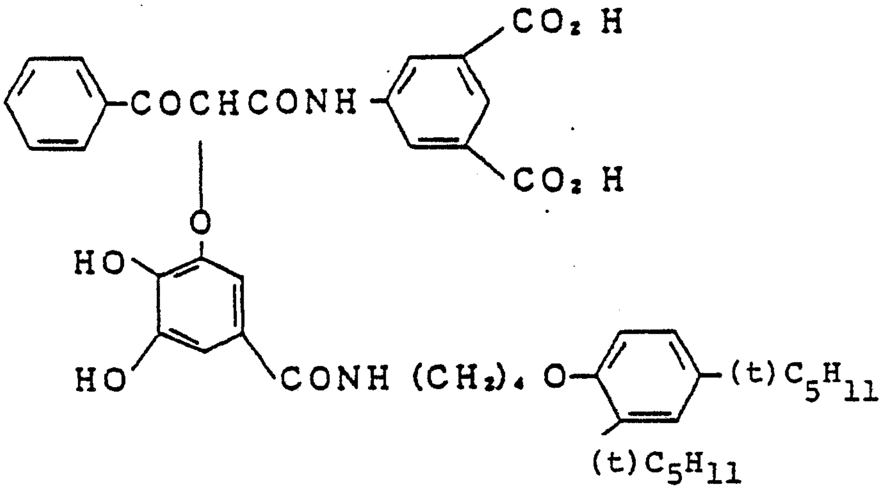
Cℓ
NHCOCH₂ CH₂ CO₂ H
O
(n)C16H31
(n)C16H31
OH

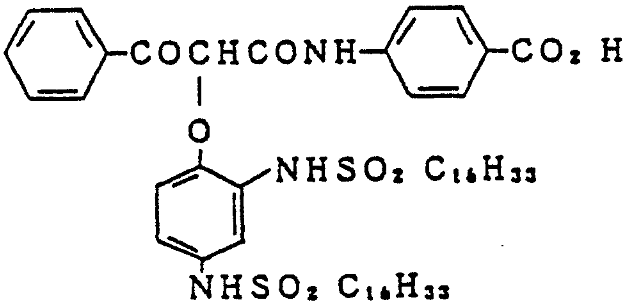
A-9


CO₂ H
OH
NHCO
CO₂ H
O
HO
C₁₅H₃₁
OH

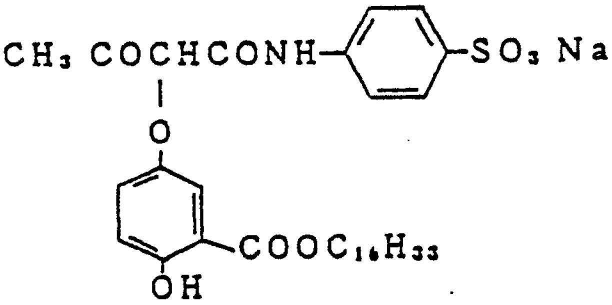
A-10



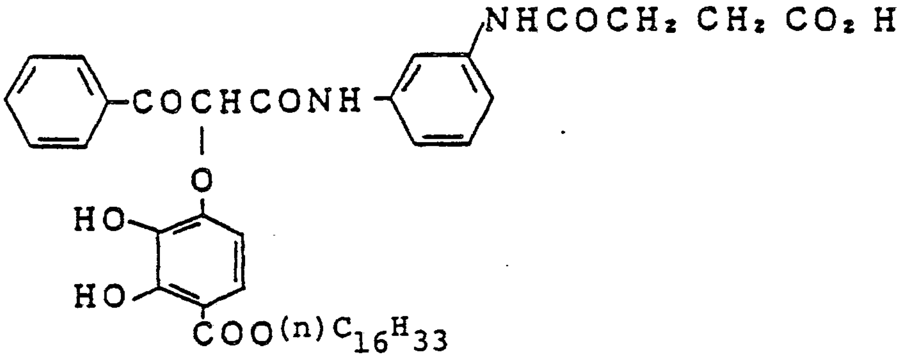
A-11



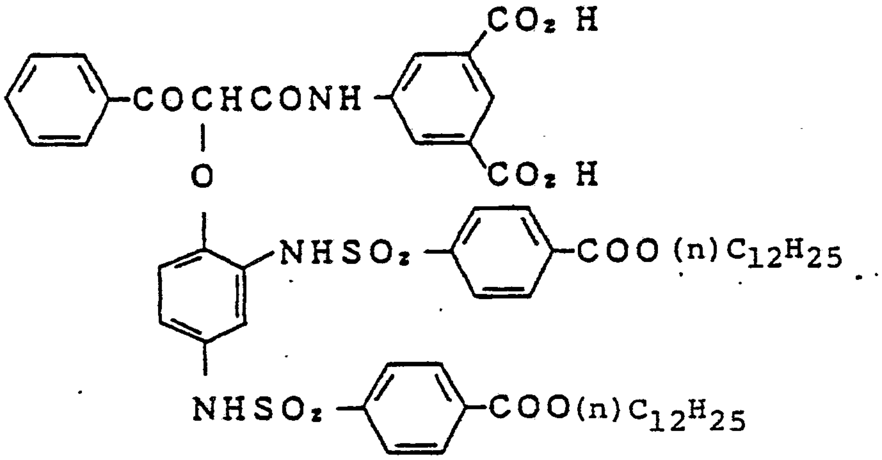
A-12



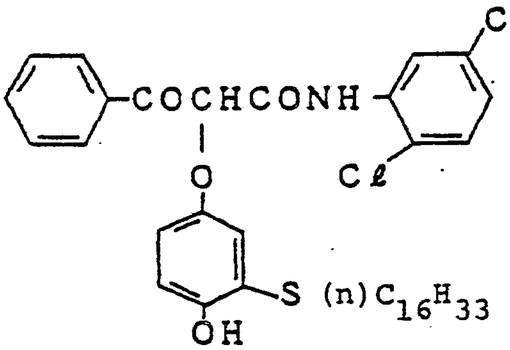
A-13



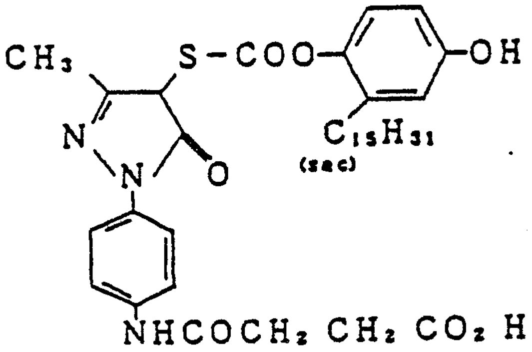
A-14



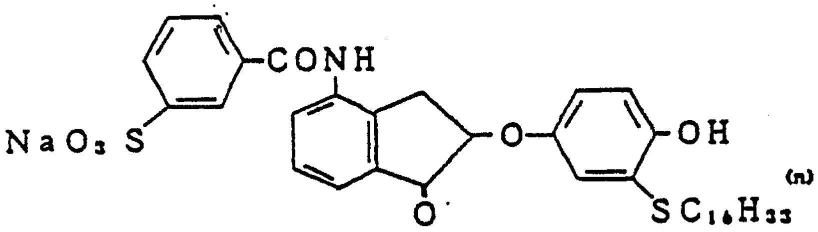
A-15



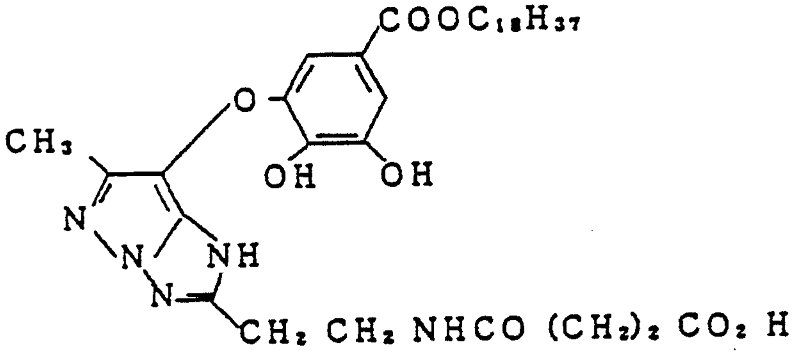
A-16


CH3
S-COO
OH
N
N
O
C15H31
(sec)
NHCOCH2 CH2 CO2 H

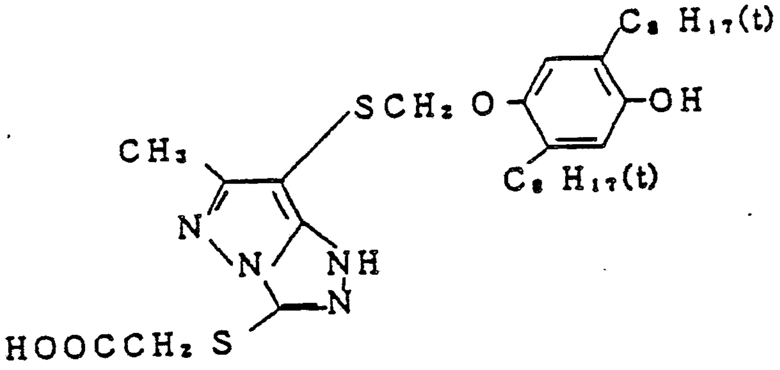
A-17


CONH
NaO3 S
O
OH
O
(n)
SC16H33

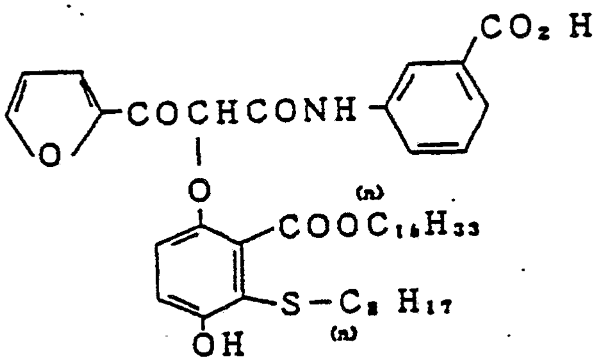
A-18


COOC18H37
O
CH3
OH
OH
N
N
NH
N
CH2 CH2 NHCO (CH2)2 CO2 H

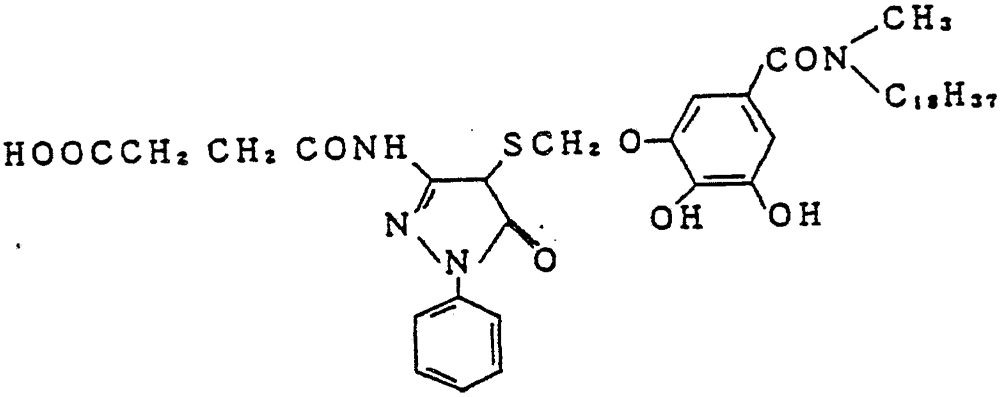
A-19



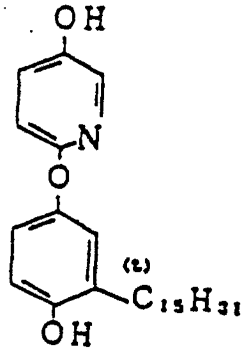
A-20



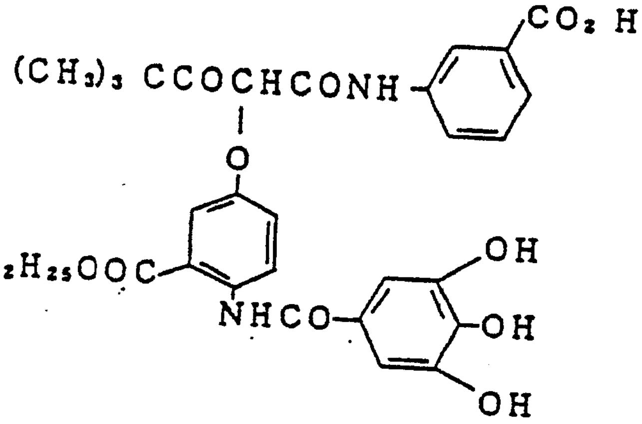
A-21



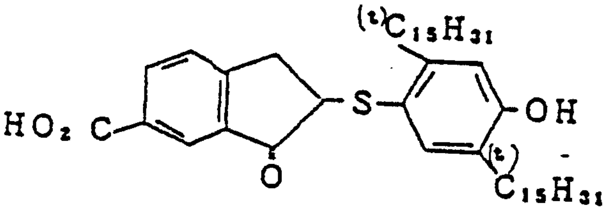
A-22


OH
N
O
(t)
C15H31
OH

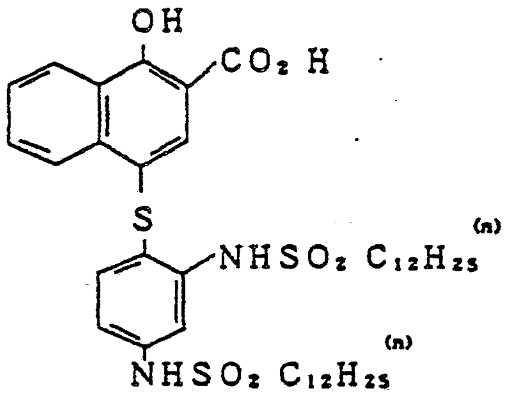
A-23


CO2 H
(CH3)3 CCOCHCONH
O
(n)
C12H25OOC
NHCO
OH
OH
OH

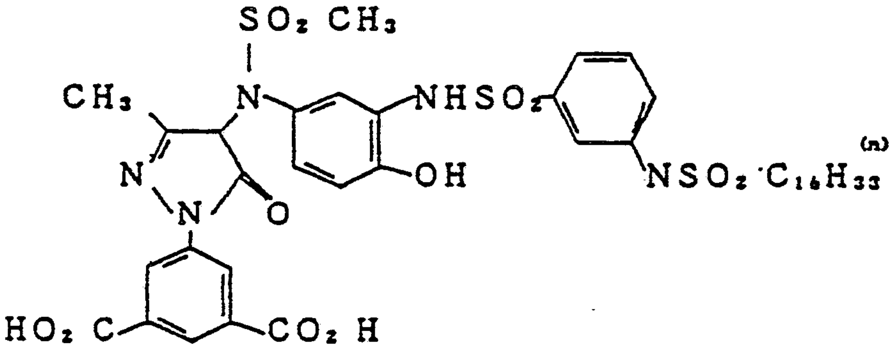
A-24


(t)C15H31
HO2 C
S
OH
O
(t)
C15H31

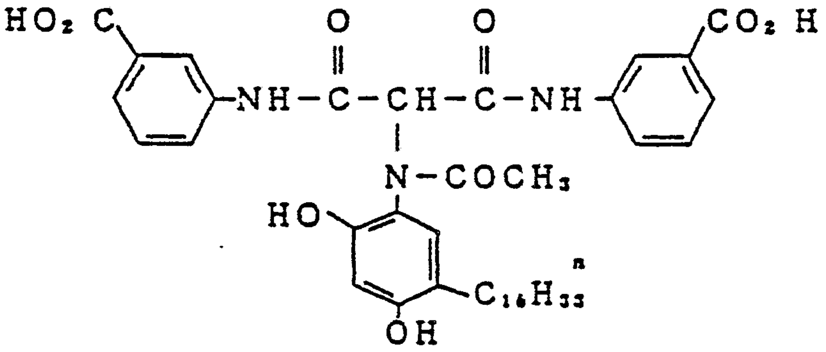
A-25



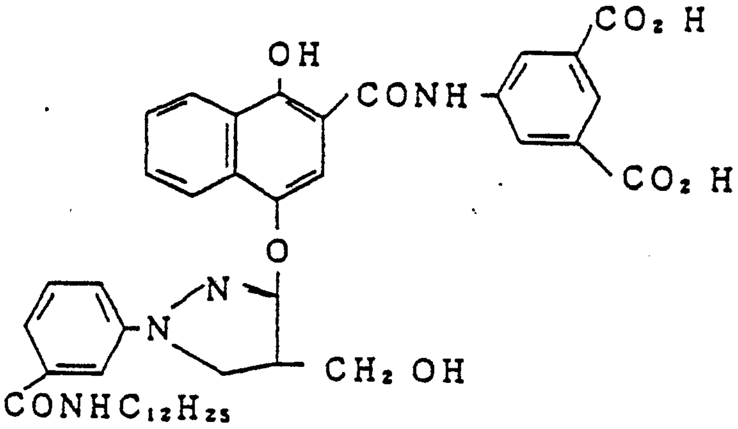
A-26



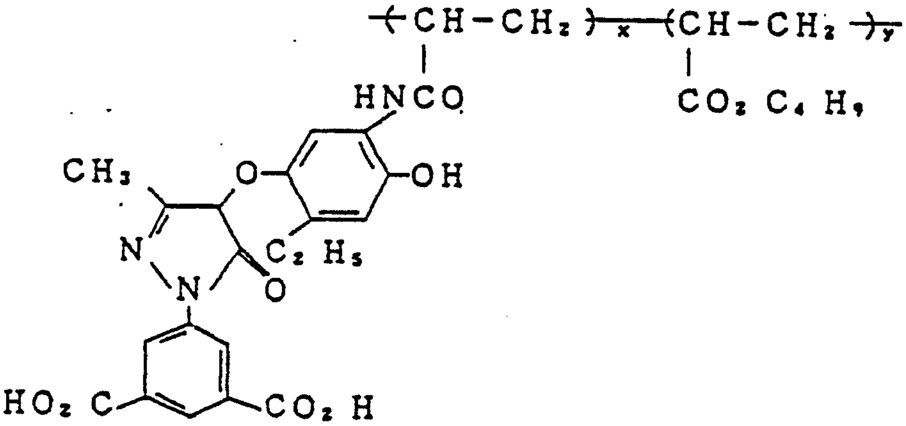
A-27



A-28



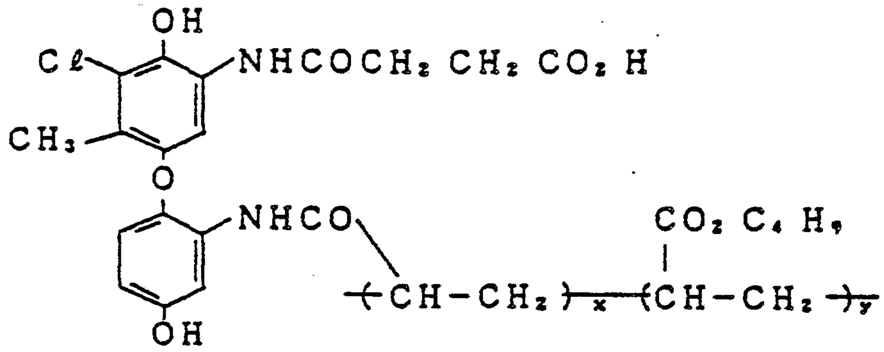
A-29



x : y = 1 : 2

Average molecular weight 20,000

A-30

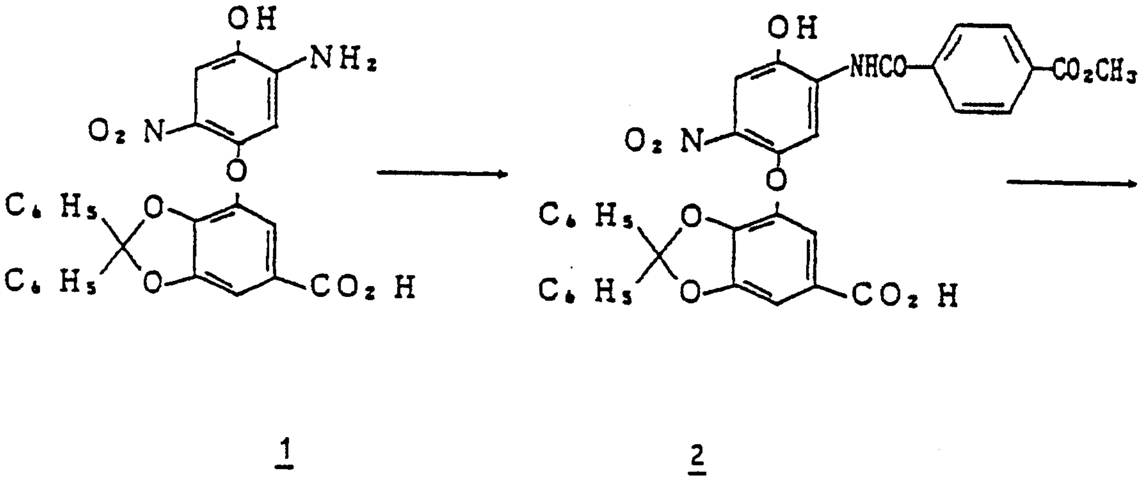


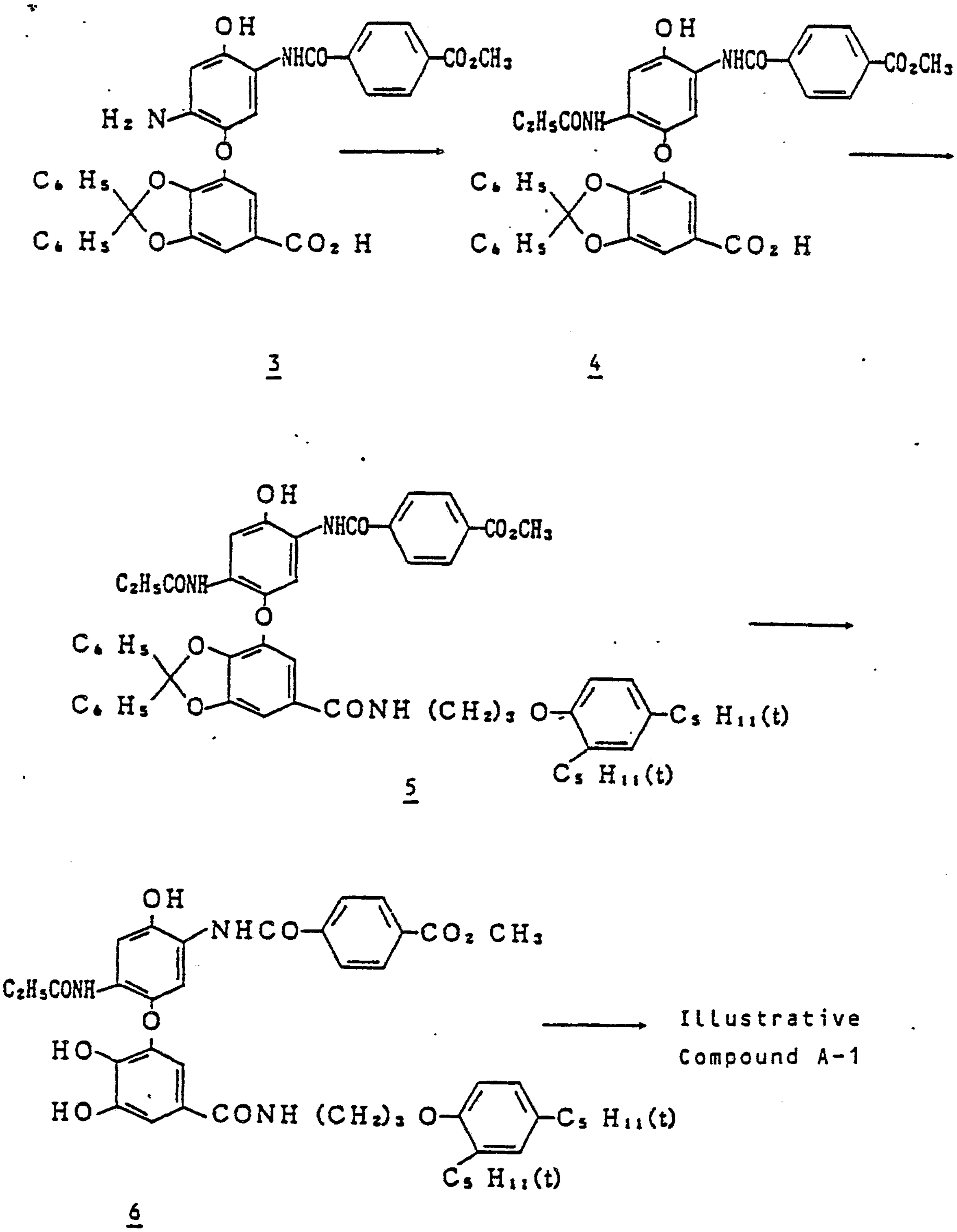
x : y = 1 : 2

Average molecular weight 15,000

Synthesis Example (1): Synthesis of Illustrative Compound A-1

This compound is synthesized by the route indicated below.





(1) Compound 1 (synthesized using the method disclosed in Japanese Patent Application (OPI) No. 233741/86) (97.0 g) and 40 g of 4-methoxycarbonylbenzoyl chloride were mixed in a mixed solvent consisting of 30 ml of pyridine and 300 ml of ethyl acetate and reacted at a temperature of 5°C or below. One liter of water was added to the reaction mixture, the oil layer was recovered using a separating funnel and 103 g of compound 2 was obtained on distilling off the solvent under reduced pressure.

(2) Compound 2 (103 g) and 100 g of iron powder were added to a solvent mixture consisting of 10 ml of acetic acid, 800 ml of isopropanol and 100 ml of water and heated under reflux for a period of 5 hours. The insoluble material was removed by filtration and the filtrate was concentrated under reduced pressure. The crystals which precipitated out were separated by filtration and 83.5 g of compound 3 was obtained.

(3) The compound 3 obtained in the way indicated above (83.5 g) and 21.1 g of propionic anhydride were added to 500 ml of ethyl acetate and reacted at room temperature (25°C) for a period of 3 hours. One liter of water was added and the mixture was transferred to a separating funnel. The oil layer was recovered after washing with water and the solvent was distilled off under reduced pressure. On recrystallizing the residue from ethyl acetate and hexane 75.6 g of compound 4 were obtained.

(4) The compound 4 obtained in the way indicated above (75.6 g) was added to 500 ml of tetrahydrofuran and 26.7 g of thionyl chloride was added dropwise while cooling in ice. After reacting for a period of 1 hour, 32.7 g of a mixture of grams of 3-(2,4-di-tert-amylphenoxy)propylamine and 30 ml of pyridine was added dropwise. After reacting for a period of 2 hours, 1 liter of ethyl acetate and 1 liter of water were added, the mixture was transferred to a separating funnel and the oil layer was recovered and washed with water until it became neutral. The oil layer was then concentrated and 77.6 g of compound 5 was obtained by crystallization with the addition of ethyl acetate and hexane to the residue.

(5) The compound 5 obtained in the way indicated above (77.6 g) was mixed with a mixture of 500 ml of methanol and 50 ml of hydrochloric acid and reacted for 2 hours at 50°C. Compound 6 (57.1 g) was obtained on working up the reaction mixture in the usual way.

(6) A mixture consisting of 57.1 g of compound 6, 12.2 g of potassium hydroxide, 100 ml of water and 500 ml of methanol was stirred for a period of 3 hours. Illus trative compound A-I (38.9 g) was obtained on subsequently working up the reaction mixture in the usual way after neutralization with hydrochloric acid.

The silver halide which is contained in the photographic emulsion layers of the photographic materials in which the invention is employed is preferably a silver iodobromide, silver iodochloride or a silver iodochlorobromide which contains less than about 30 mol% of silver iodide. Silver iodobromides which contain from about 2 mol% to about 25 mol% of silver iodide are especially desirable.

The silver halide grains in the photographic emulsion may have a regular crystalline form, such as a cubic, octahedral or tetradecahedral form, an irregular crystalline form such as a spherical or plate-like form, they may have crystal defects such as twinned crystal planes, etc., or they may have a complex form incorporating these forms.

The silver halide grain size may be such as to include fine grains of less than about 0.2 microns and large grains of which the projected area diameter reaches about 10 microns and they may be in the form of a polydisperse emulsion or a mono-disperse emulsion.

The silver halide photographic emulsions which can be used in the invention can be prepared using the methods disclosed, for example, in Research Disclosure (RD) No. 17643 (December, 1978), pages 22-23, "I. Emulsion Prepara tion" (Emulsions preparation and types) and RD No. 18716 (November, 1979), page 648, and the methods described by P. Glafkides in Chimie et Physique Photographique, Paul Montel, 1967, by G.F. Duffin in Photographic Emulsion Chemistry, Focal Press, 1966, and by Zelikman et al. in Making and Coating Photographic Emulsion, Focal Press, 1964, etc.

The mono-disperse emulsion disclosed in U.S. Patents 3,574,628 and 3,655,394 and in British Patent 1,413,748 are preferred.

Furthermore, plate-like grains such that the aspect ratio is greater than about 5 can be used in the invention. Plate-like grains can be prepared easily using the method disclosed by Gutoff on pages 248-257 of volume 14 of Photographic Science and Engineering (1970), and the methods disclosed in U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520 and in British Patent 2,112,157, etc.

The crystal structure may be uniform or the inner and outer parts may have a different halogen composition to provide a layered type of structure. Furthermore, the silver halides of different compositions may be joined, for example, with an epitaxial junction, or they may be joined with a compound other than silver halide such as silver thiocyanate or lead oxide.

Mixtures of grains of various crystal forms can also be used.

Silver halide emulsions which have been physically ripened, chemically ripened and spectrally sensitized.are normally used. The additives used in processes of this type are disclosed in Research Disclosure Nos. 17643 and 18716 and the locations of these materials in the said publications are summarized in the table below.

Known photographic additives which can be used in the invention are also disclosed in the two research disclosures indicated above and the locations of the related disclosures are shown in the following table.

	Type of Additives	RD 17643	RD 18716
1.	Chemical Sensitizers	p. 23	p. 648, right column
2.	Speed increasing agents		As above
3.	Spectral Sensitizers Strong Color Sensitizers	pp. 23-24	from p. 648, right column to p. 649, right column
4.	Whiteners	p. 24	
5.	Anti-foggants and Stabilizers	pp. 24-25	p. 649, right column
6.	Light absorbers, filter dyes, UV Absorbers	pp. 25-26	from p. 649, right column to p. 650, left comumn
7.	Anti-staining agents	p. 25, right column	p. 650, from left to right column
8.	Dye image stabilizers	p. 25	
9.	Film hardening agents	p. 26	p. 651, left column
10.	Binders	p. 26	As above
11.	Plasticizers, Lubricants	p. 27	p. 650, right column
12.	Coating promotors, Surfactants	pp. 26-27	As above
13.	Anti-static agents	p. 27	As above

Various color couplers can be used in the invention and actual examples are disclosed in the patents disclosed in Research Disclosure (RD) No. 17643, VII-C to G.

The preferred yellow couplers are those disclosed, for example, in U.S. Patents 3,933,501, 4,022,620, 4,326,024 and 4,401,752, Japanese Patent Publication No. 10739/83 and British Patents 1,425,020 and 1,476,760, etc.

5-Pyrazolone and pyrazoloazole based compounds are preferred for the magenta couplers and those disclosed in U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June, 1984), Japanese Patent Application (OPI) No. 33552/85, Research Disclosure No. 24230 (June, 1984), Japanese Patent Application (OPI) No. 43659/85 and U.S. Patents 4,500,630 and 4,540,654, etc. are especially desirable.

Phenol and naphthol based couplers are used as cyan couplers and those disclosed in U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, 4,327,173, 3,446,622, 4,333,999, 4,451,559 and 4,427,767, West German Patent Laid Open No. 3,329,729, European Patents 121,365A and 161,626A, etc. are preferred.

The colored couplers for correcting the unrequired absorptions of the colored dyes disclosed in section VII-G of Research Disclosure No. 17643, U.S. Patent 4,163,670, Japanese Patent Publication No. 39413/82, U.S. Patents 4,004,929 and 4,138,258 and British Patent 1,146,368 are preferred.

Those couplers disclosed in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570 and West German Patent (Laid Open) No. 3,234,533 are preferred as couplers of which the colored dye has suitable diffusion properties.

Typical examples of polymerized dye forming couplers are disclosed in U.S. Patents 3,451,820, 4,080,211 and 4,367,282 and in British Patent 2,102,173, etc.

The use of couplers which release residual groups which are useful photographically on coupling is preferred in this invention. The DIR couplers which release development inhibitors disclosed in the patents disclosed in sections VII-F of the aforementioned Research Disclosure (RD) No. 17643, Japanese Patent Application (OPI) Nos. 151944/82, 154234/82 and 184248/85 and U.S. Patent 4,248,962 are preferred.

Those couplers which release nucleating agents or development accelerating agents in the form of the image during development which are disclosed in British Patents 2,097,140 and 2,131,188 and in Japanese Patent Application (OPI) Nos. 157638/84 and 170840/84 are preferred.

Other couplers which can be used in the light sensitive materials of this invention include the competitive couplers disclosed in U.S. Patent 4,130,427, etc., the polyequivalent couplers disclosed in U.S. Patents 4,283,472, 4,338,393 and 4,310,618, etc., the DIR redox compound releasing couplers disclosed in Japanese Patent Application (OPI) No. 185950/85, etc. and the coulers which release a dye of which the color is restored after elimination as disclosed in European Patent 173,302A.

The couplers used in the invention can be introduced into the photosensitive material using the various known methods of dispersion.

Examples of the high boiling point solvents which can be used in the oil in water dispersion method are disclosed in U.S. Patent 2,322,027, etc.

Actual examples of the processes and effects of the latex dispersion method and of latexes for impregnation purposes have been disclosed in U.S. Patent 4,199,363 and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230, etc.

Suitable supports which can be used in the invention are disclosed, for example, on page 28 of the aforementioned Research Disclosure (RD) No. 17643 and in the section from the right hand column of page 647 to the left hand column on page 648 of Research Disclosure (RD) No. 18716.

Color photographic materials in accordance with this invention can be developed using the normal methods of development as disclosed on pages 28 and 29 of the aforementioned Research Disclosure - (RD) No. 17643 and in the section from the left hand column to the right hand column of page 651 of Research Disclosure (RD) No. 18716.

A color developer which is used for the development of the color photographic materials of this invention is an alkaline aqueous solution preferably containing an aromatic primary amine color developing agent as the main component. As the color developing agent, an aminophenolic compound may be useful but a p-phenylenediamine series compound is preferably used. Typical examples thereof are 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesul fonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline and the sulfates, hydrochlorides, or p-toluenesulfonates of them. They can be used singly or as a mixture thereof.

The color developer generally contains a pH buffer such as the carbonates, borates, or phosphates of an alkali metal and a development inhibitor or an antifoggant such as bromides, iodides, benzimidazoles, benzothiazoles, and mercapto compounds. Also, if necessary, the developer may contain various preservatives such as hydroxylamine, diethylhydroxylamine, sulfites hydrazines, phenylsemicarbazides, triethanolamine, catecholsulfonic acids, triethylenediamine-(1,4-diazabicyclo[2,2,2]octanes, etc.; organic solvents such as ethylene glycol, diethylene glycol, etc.; development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salt, amines, etc.; dye forming couplers, competing couplers, fogging agents such as sodium borohydride, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, etc.; tackifiers; chelating agents such as aminopolycarboxylic acid, aminopolyphosphonic acid, alkyl-phosphonic acid, phosphonocarboxylic acid, etc. (e.g., ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N′,N′-tetra methylenephosphonic acid, ethylene-di(o-hydroxyphenylacetic acid) and the salts thereof).

Also, in the case of performing reversal processing, a black and white development is usually performed before the color development. For the black and white developer, dihydroxybenzenes such as hydroquinone, etc., 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, etc., and aminophenols such as N-methyl-p-aminophenol, etc., can be used singly or as a combination thereof.

The pH of the color developer and black and white developer is generally from 9 to 12. Also, the amount of the replenishers for these developers depends upon the kind of color photographic material being used but is generally less than 3 liters per square meters of the color photographic material. The amount thereof can be reduced below 500 ml by reducing the bromide ion concentration in the replenisher. In the case of reducing the amount of replenisher, it is preferred to reduce the contact area of the surface of the processor with air for preventing the evaporation of liquid and occurrence of the air oxidation of liquid. Also, by employing a means for preventing the deposition of bromide ions in the developer, the amount of the replenisher can be reduced.

The photographic emulsion layers after color development are generally bleached. The bleach processing may be performed simultaneously with (bleach-fix or blix processing) or separately from a fix processing. Furthermore, for quickening the processing, blix processing may be performed after bleaching. Moreover, processing of continuous blixing using two tanks, fixing before blixing, or bleaching after blixing may be performed according to the purposes.

As the bleaching agent, compounds of multivalent metals such as iron (III), cobalt (III), chromium (IV), copper (II), etc., as well as peroxides, quinones, nitro compounds are used. Typical bleaching agents are ferricyanides, perchromates, organic complex salts of iron (III) or cobalt (III), such as the complex salts of aminipolycarboxylic acids, such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, glycol ether diaminetetraacetic acid, etc., or citric acid, tartaric acid, malic acid, etc., persulfates, bromates, permanganates, nitrobenzenes, etc.

In these compounds, ethylenediaminetetraacetic acid iron (III) complex salts as well as aminopolycarboxylic acid iron (III) complex salts and persulfates are preferred from the viewpoint of quick processing and prevention of environmental pollution. Furthermore, aminopolycarboxylic acid iron (III) complex salts are particularly useful for bleach solution and blix solution.

The pH of the blix solution using the aminopolycarboxylic acid iron (III) complex salt is usually from 5.5 to 8 but the pH may be further lowered for quickening the processing.

For the bleach solution, blix solution or the prebath thereof, a bleach accelerator can be, if necessary, used. Specific examples of such bleach accelerators are compounds having a mercapto group or disulfide group described in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, Japanese Patent Application (OPI) Nos. 32736/78, 57..1/78, 37418/78, 72623/78, 95630/78, 95631/78, 10423/78, 124424/78, 141623/78, and 28426/78, Research Disclosure, No. 17129 (July, 1978), etc.; thiazolizine derivatives described in Japanese Patent Application (OPI) No. 140129/85; thiourea derivatives described in Japanese Patent Publication No. 8506/70, Japanese Patent Application (OPI) Nos. 20832/77 and 32735/78, U.S. Patent 3,706,561; iodides described in West German Patent 1,127,715 and Japanese Patent Application (OPI) No. 16235/83; polyoxyethylene compounds described in West German Patents 966,410 and 2,748,430; polyamine compounds described in Japanese Patent Publication No. 8836/70; other compounds described in Japanese Patent Application (OPI) Nos. 42434/74, 59644/74, 94927/78, 35727/79, 26506/80, and 163940/83; and also bromide ions.

In these compounds, the compounds having a mercapto group or a disulfide group are preferred from the viewpoint of obtaining a high accelerating effect and in particular, the compounds described in U.S. patent 3,893,858, West German Patent 1,290,812, and Japanese Patent Application (OPI) No. 95630/78 are preferred. Furthermore, the compounds described in U.S. Patent 4,552,834 are preferably used in this invention.

The bleach accelerator may be incorporated in the color photographic materials of this invention. These bleach accelerators are particularly useful in the case of blixing color photographic materials for photographing.

As the fixing agent, there are thiosulfates, thiocyanates, thioether series compounds, thioureas, a large amount of iodides but thiosulfate are generally used and in particular, ammonium thiosulfate is most widely used.

As a preservative for the blix solution, a sulfite, a hydrogensulfite, or a carbonyl hydrogensulfite is preferred.

The silver halide color photographic material is generally washed and/or stabilized after desilvering.

The amount of wash water for the wash step can be widely changed according to various conditions such as the characteristics (e.g., the kind of the couplers, etc.) of the color photographic materials, the washing temperature, the number (stage number) of wash tanks, the replenisher system such as a countercurrent system or ordinary current system, and others. In this case, the relation between the number of wash tanks and the amount of water in the multistage countercurrent system can be determined by the method shown in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, 248-253 (May, 1955).

By the aforesaid multistage countercurrent system, the amount of wash water can be greatly reduced but there occurs a problem of drawing bacteria and attaching of floats thus formed on the light-sensitive materials by the increase of retension time.

In the processing of the color photographic materials of this invention, the methods of reducing calcium ions and magnesium ions described in Japanese Patent Application No. 131632/86 can be very effectively used for resolving such problems in the processing of the color photographic materials of this invention.

Also, isothiazolone compounds and cyabendazoles described in Japanese Patent Application (OPI) No. 8542/82, chlorine series sterilizers such as chlorinated sodium isocyanurate, etc., and other sterilizers such as benzotriazoles, etc., described in Hiroshi Horiguchi, Bokin Bobaizai no Kagaku (Chemistry of Antibacterial and Antifungal Agents), Biseibutsu no Mekkin, Sakkin, Bobai Gijitsu (Sterillizing, and Antifungal Techniques of Microorganisms), edited by the society of Sanitary Technique, Bokin Bobai Zai Jiten (Handbook of Antibacterial and Antifungal Agents), edited by Antibacterial and Angifungal Society of Japan can be used.

The pH of wash water in processing of the color photographic materials of this invention is of from 4 to 9, and preferably from 5 to 8. The washing temperature and washing time can be desirably selected according to the characteristics and uses of the light-sensitive materials of this invention but are generally in the ranges of from 15 to 45°C and from 20 seconds to 10 minutes, and preferably from 25 to 40°C and 30 seconds to 5 minutes.

Furthermore, the color photographic materials of this invention can be directly subjected to a stabilization processing in place of the aforesaid wash process. For such stabilization processing, known methods described in Japanese Patent Application (OPI) Nos. 8543/82, 14834/83, and 220345/85 can be all used.

Also, after the aforesaid wash processing, the color photographic materials are, as the case may be, further stabilized and as such an example, there are a stabilization bath containing formalin and a surface active agent, which is used as the final bath for color photographic materials for photographing. Such a stabilizing bath can contain a chelating agent and an antifungal agent.

The overflow liquid obtained with the replenishing of the aforesaid wash and/or stabilization liquid can be reused in a desilvering step and other steps.

The silver halide color photographic materials of this invention may contain a color developing agent for simplifying and quickening processing. For the incorporation, it is preferred to use various precursors for color developing agent. Examples thereof are Sciff base type compounds described in U.S. Patent 3,342,599 and Research Disclosure Nos. 14850 and 15159, indoaniline series compounds described in U.S. Patent 3,342,597, also compounds described in Research Disclosure, No. 13924, metal complexes described in U.S. Patent 3,719,492, and urethane compounds described in Japanese Patent Application (OPI) No. 135628/78.

The silver halide color photographic materials of this invention may further contain various kinds of 1-phenyl-3-pyrazolidones for accelerating color development. Typical compounds are described in Japanese Patent Application (OPI) Nos. 64339/81, 144547/82, and 115438/83.

Various processing solutions in this invention are used at from 10°C to 50°C. The standard processing temperature is from 33°C to 38°C but a higher temperature may be employed for quickening the processing and a lower temperature may be employed for improving the image quality and stability of processing solutions. Also, for saving silver, processing using a cobalt intensification or hydrogen peroxide intensification described in West German Patent 2,226,770 and U.S. Patent 3,674,499 may be performed.

The invention is illustrated below by means of detailed examples but the invention is not limited by these examples. Unless otherwise indicated herein, all parts, percents, ratios and the like are by weight.

EXAMPLE 1

Sample 101, a multi-layer color photographic material consisting of each of the layers of which the compositions are indicated below on an undercoated cellulose triacetate film support was prepared in order to evaluate the effectiveness of the compounds of this invention.

Preparation of Sample 101

The amount of the sensitizing dyes used are expressed as the number of mols per mol of silver halide which is present in the same layer.

First Layer (Anti-halation Layer)

Black Colloidal Silver	0.2 g/m^2
Gelatin	1.3 g/m^2
Colored Coupler C-1	0.06 g/m^2
Ultraviolet Absorber UV-1	0.1 g/m^2
Ultraviolet Absorber UV-2	0.2 g/m^2
High Boiling Point Organic Solvent Oil-1	0.01 cc/m^2
High Boiling Point Organic Solvent Oil-2	0.01 cc/m^2

Second Layer (Intermediate Layer)

Fine Silver Bromide Grains (average grain diameter 0.07μm)	0.15 g/m^2
Gelatin	1.0 g/m^2
Colored Coupler C-2	0.02 g/m^2
High Boiling Point Organic Solvent Oil-1	0.1 cc/m^2

Third Layer (Low Speed Red-Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (2 mol% silver iodide, average grain size 0.3μm)	0.4 g/m^2 as silver
Gelatin	0.6 g/m^2
Sensitizing Dye I	1.0×10^{-4}
Sensitizing Dye II	3.0×10^{-4}
Sensitizing Dye III	1.0×10^{-4}
Coupler C-3	0.06 g/m^2
Coupler C-4	0.06 g/m^2
Coupler C-8	0.04 g/m^2
Coupler C-2	0.03 g/m^2
High Boiling Point Organic Solvent Oil-1	0.03 cc/m^2
High Boiling Point Organic Solvent Oil-3	0.012 cc/m^2

Fourth Layer (Medium Speed Red-Sensitive Emulsion Layer)

Silver Iodobromide Emulsion (5 mol% silver iodide, average grain size 0.5μm)	0.7 gm^2 as silver
Sensitizing Dye I	1.0×10^{-4}
Sensitizing Dye II	3.0×10^{-4}
Sensitizing Dye III	1.0×10^{-4}
Gelatin	2.5 g/m^2
Coupler C-3	0.24 g/m^2
Coupler C-4	0.24 g/m^2
Coupler C-8	0.04 g/m^2
Coupler C-2	0.04 g/m^2
High Boiling Point Organic Solvent Oil-1	0.15 cc/m^2
High Boiling Point Organic Solvent Oil-3	0.02 cc/m^2

Fifth Layer (High Speed Red-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (10 mol% silver iodide, average grain size 0.7 µ) 1.0 g/m^2 as silver
Gelatin 1.0 g/m^2 Sensitizing Dye I 1.0×10^{-4}
Sensitizing Dye II 3.0×10^{-4}
Sensitizing Dye III 1.0×10^{-4}
Coupler C-6 0.05 g/m^2
Coupler C-7 0.1 g/m^2
High Boiling Point Organic Solvent Oil-1 0.01 cc/m^2
High Boiling Point Organic Solvent Oil-3 0.05 cc/m^2

Sixth Layer (Intermediate Layer)Gelatin 1.0 g/m^2
Compound Cpd-A 0.03 g/m^2
High Boiling Point Organic Solvent Oil-1 0.05 cc/m^2

Seventh Layer (Low Speed Green-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (4 mol% silver iodide, average grain size 0.3 µ) 0.30 g/m^2 as silver
Sensitizing Dye IV 5.0×10^{-4}
Sensitizing Dye VI 0.3×10^{-4}
Sensitizing Dye V 2.0×10^{-4}
Gelatin 1.0 g/m^2
Coupler C-9 0.2 g/m^2
Coupler C-5 0.03 g/m^2
Coupler C-1 0.03 g/m^2
High Boiling Point Organic Solvent Oil-1 0.5 cc/m^2

Eighth Layer (Medium Speed Green-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (5 mol% silver iodide, average grain size 0.5 µ) 0.4 g/m^2 as silver
Sensitizing Dye IV 5.0×10^{-4}
Sensitizing Dye V 2.0×10^{-4}
Sensitizing Dye VI 0.3×10^{-4}
Coupler C-9 0.25 g/m^2
Coupler C-1 0.03 g/m^2
Gelatin 0.8 g/m^2
Coupler C-10 0.15 g/m^2
Coupler C-5 0.01 g/m^2
High Boiling Point Organic Solvent Oil-1 0.2 cc/m^2

Ninth Layer (High Speed Green-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (6 mol% silver iodide, average grain size 0.7 µ) 0.85 g/m^2 as silver
Gelatin 1.0 g/m^2
Sensitizing Dye VII 3.5×10^{-4}
Sensitizing Dye VIII 1.4×10^{-4}
Coupler C-11 0.01 g/m^2
Coupler C-12 0.03 g/m^2
Coupler C-13 0.20 g/m^2
Coupler C-1 0.02 g/m^2
Coupler C-15 0.02 g/m^2
High Boiling Point Organic Solvent Oil-1 0.20 cc/m^2
High Boiling Point Organic Solvent Oil-2 0.05 cc/m^2

Tenth Layer (Yellow Filter Layer)Gelatin 1.2 g/m^2
Yellow Colloidal Silver 0.08 g/m^2
Compound Cpd-B 0.1 g/m^2 High Boiling Point Organic Solvent Oil-1 0.3 cc/m^2

Eleventh Layer (Low Speed Blue-Sensitive Emulsion Layer)Mono-disperse Silver Iodobromide Emulsion (4 mol% silver iodide, average grain size 0.3 μ) 0.4 g/m^2
Gelatin 1.0 g/m^2
Sensitizing Dye IX 2.0×10^{-4}
High Boiling Point Organic Solvent Oil-1 0.2 cc/m^2

Twelfth Layer (High Speed Blue-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (10 mol% silver iodide, average grain size 1.5 μ) 0.5 g/m^2 as silver
Gelatin 0.6 g/m^2
Sensitizing Dye IX 1.0×10^{-4}
Coupler C-14 0.25 g/m^2
High Boiling Point Organic Solvent Oil-1 0.07 cc/m^2

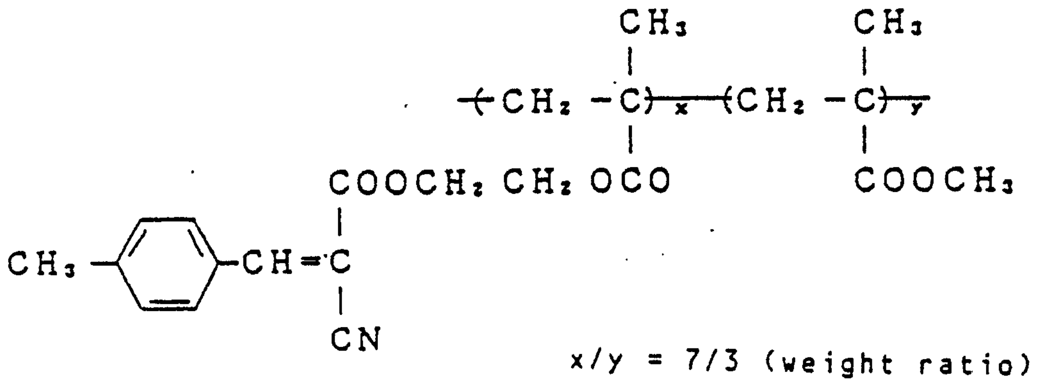
Thirteenth Layer (First Protective Layer)Gelatin 0.8 g/m^2
Ultraviolet absorber UV-1 0.1 g/m^2
Ultraviolet absorber UV-2 0.2 g/m^2
High Boiling Point Organic Solvent Oil-1 0.01 cc/m^2
High Boiling Point Organic Solvent Oil-2 0.01 cc/m^2

Fourteenth Layer (Second Protective Layer)Fine Grain Silver Bromide (average grain size 0.07 μ) 0.5 g/m^2
Gelatin 0.45 g/m^2
Poly(methylmethacrylate) grains (diameter 1.5 μ) 0.2 g/m^2
Film Hardener H-1 0.4 g/m^2
Formaldehyde Scavenger S-1 0.5 g/m^2
Formaldehyde Scavenger S-2 0.5 g/m^2

A surfactant was added as a coating promotor to each layer as well as the components indicated above. The sample prepared in the way outlined above was sample 101.

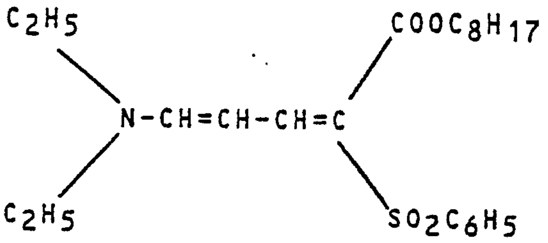
The chemical formulae or chemical names of the compounds used in the invention are indicated below.

UV-1



x/y = 7/3 (weight ratio)

UV-2

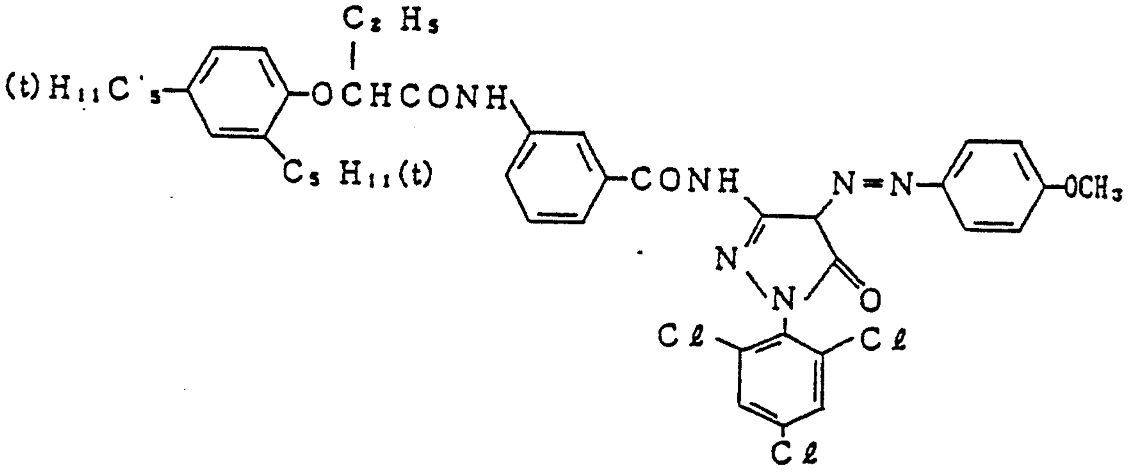


Oil-1 Tricresyl phosphate

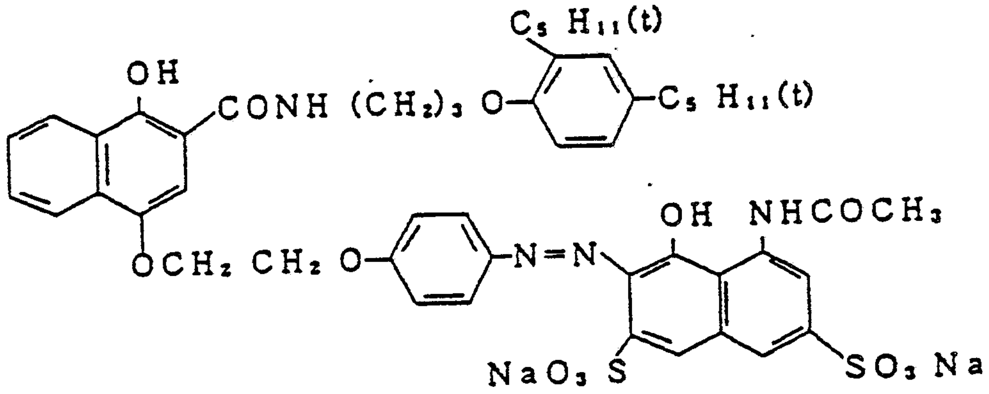
Oil-2 Dibutyl phthalate

Oil-3 Bis(2-ethylhexyl) phthalate

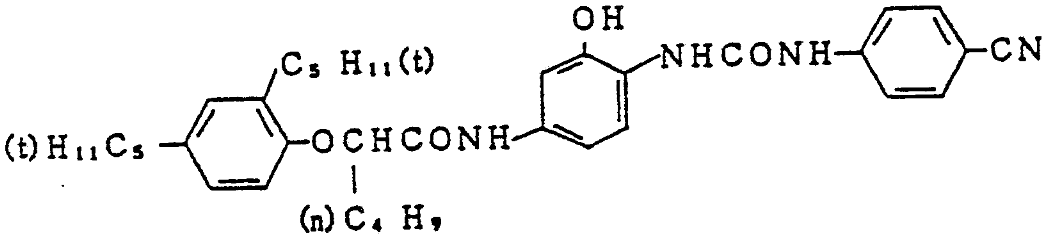
C-1



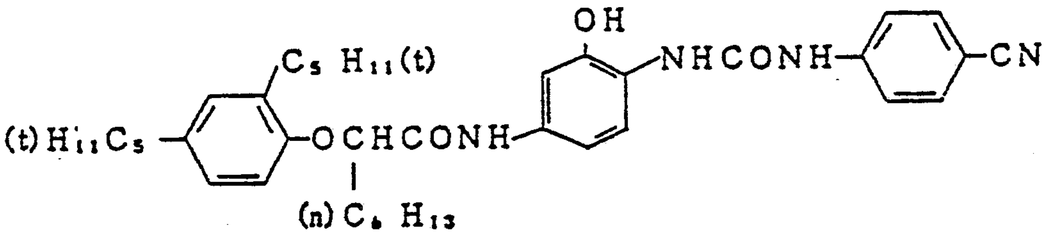
C-2



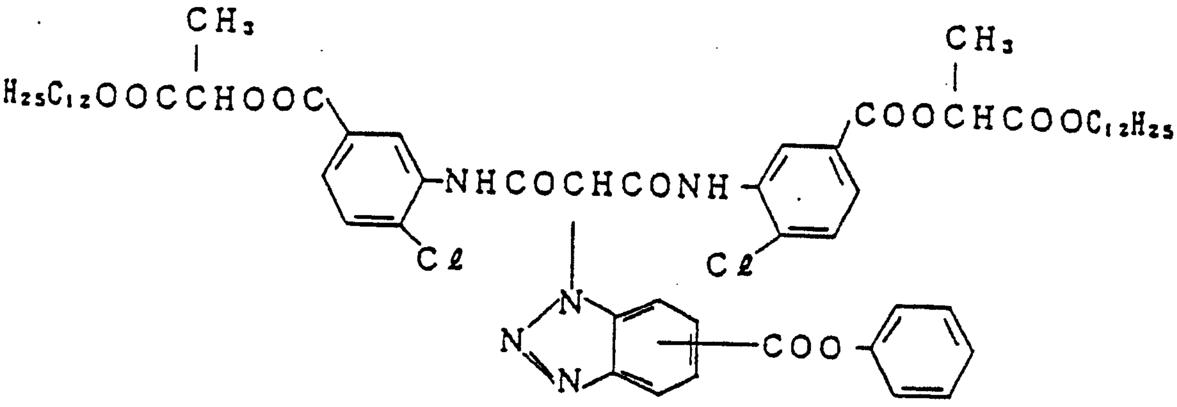
C-3



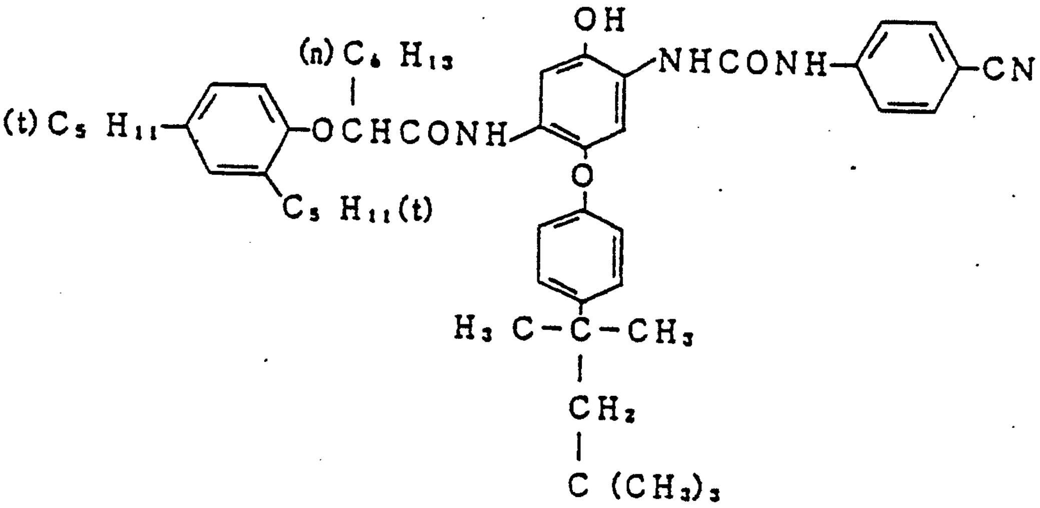
C-4



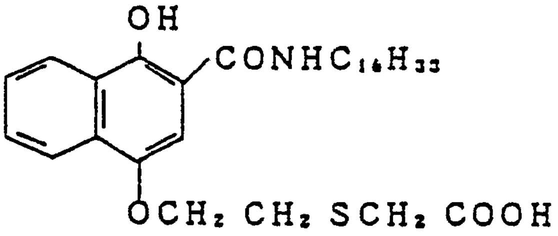
C-5


CH₃
H₂₅C₁₂OOCCHOOC
NHCOCHCONH
CH₃
COOCHCOOC₁₂H₂₅
Cℓ
Cℓ
N
N
N
COO

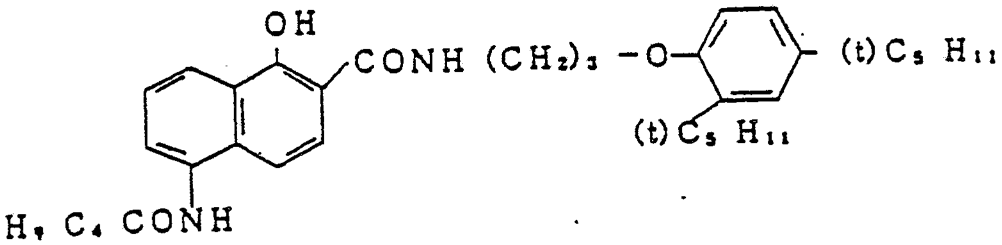
C-6


OH
(n)C₆ H₁₃
NHCONH
CN
(t)C₅ H₁₁
OCHCONH
C₅ H₁₁(t)
O
H₃ C−C−CH₃
CH₂
C (CH₃)₃

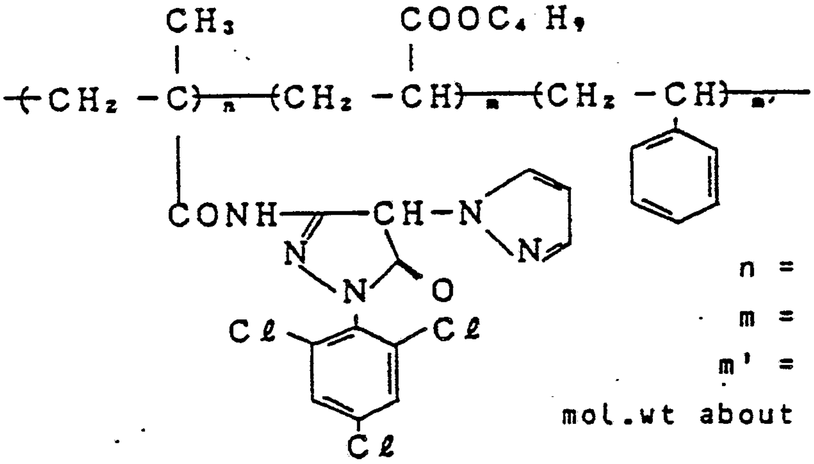
C-7


OH
CONHC₁₆H₃₃
OCH₂ CH₂ SCH₂ COOH

C-8

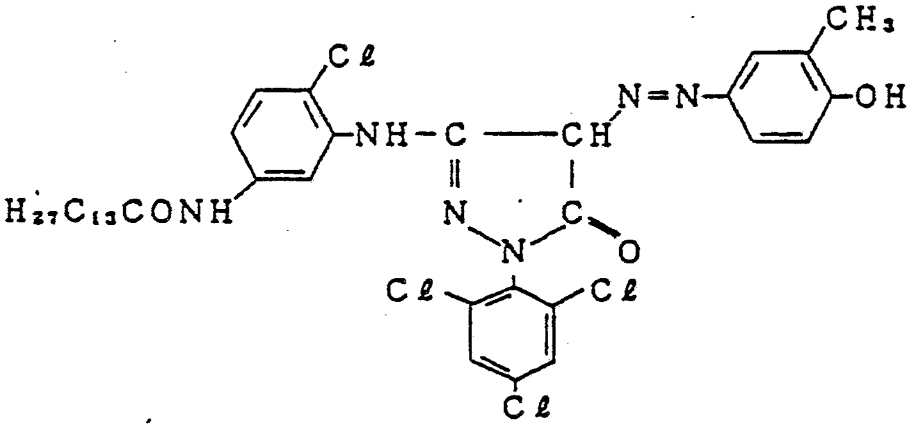


C-9

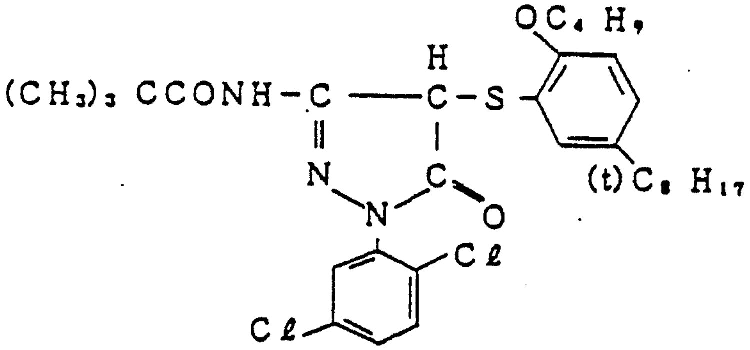


n = 50
m = 25
m' = 25
mol.wt about 20,000

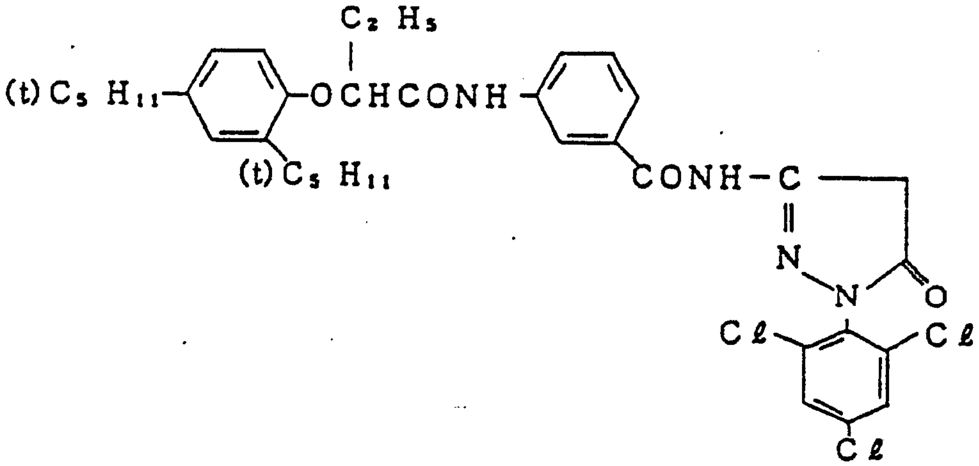
C-10



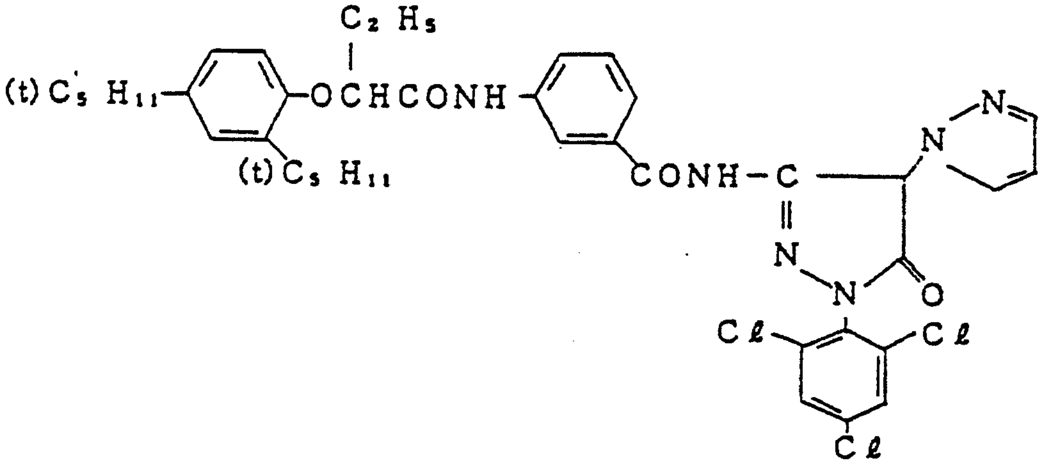
C-11


OC₄H₉
H
(CH₃)₃CCONH-C
C-S
N
N
C
O
(t)C₈H₁₇
Cℓ
Cℓ

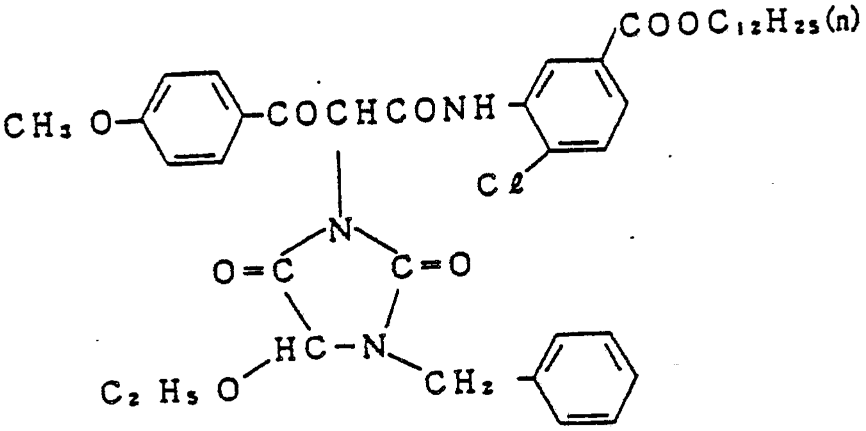
C-12


C₂H₅
(t)C₅H₁₁
OCHCONH
(t)C₅H₁₁
CONH-C
N
N
O
Cℓ
Cℓ
Cℓ

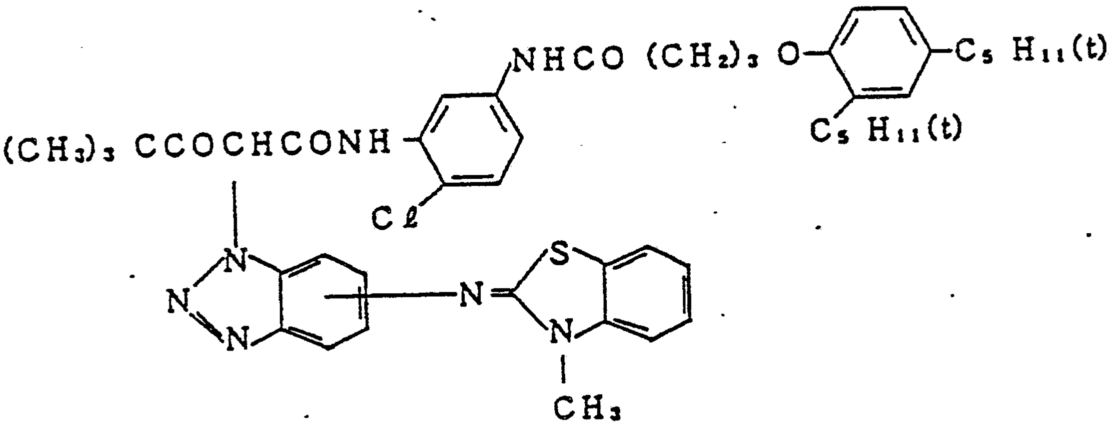
C-13


C₂H₅
(t)C₅H₁₁
OCHCONH
(t)C₅H₁₁
CONH-C
N
N
N
N
O
Cℓ
Cℓ
Cℓ

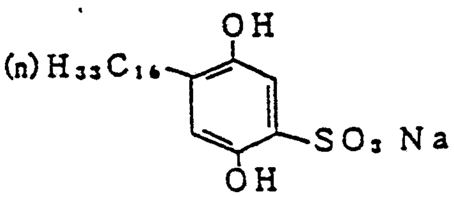
C-14



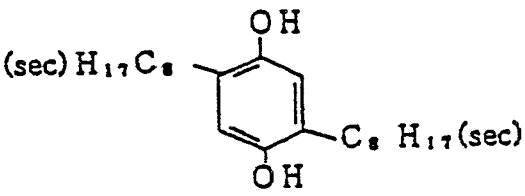
C-15



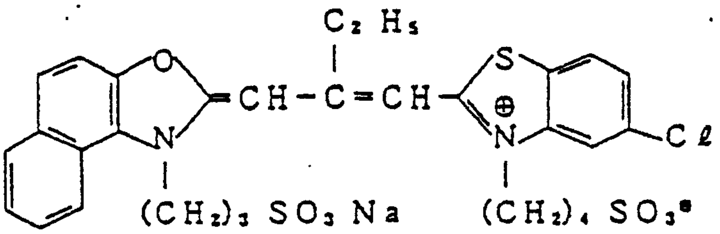
Cpd A



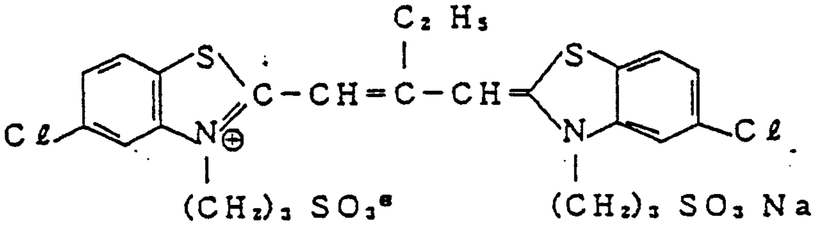
Cpd B



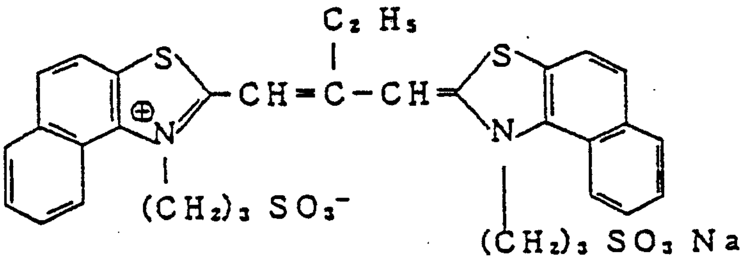
Sensitizing Dye I



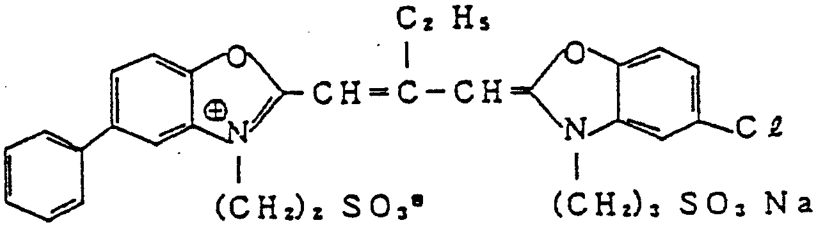
Sensitizing Dye II



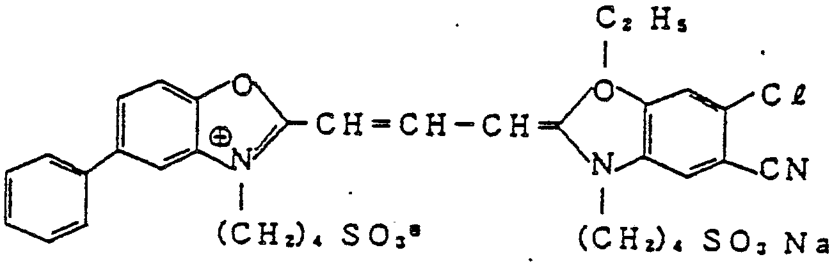
Sensitizing Dye III



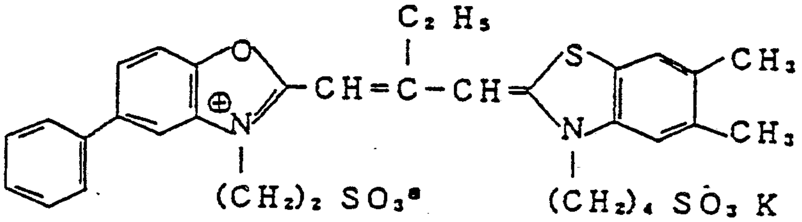
Sensitizing Dye IV



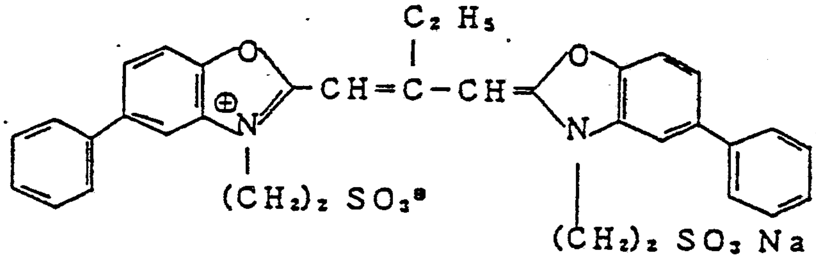
Sensitizing Dye V



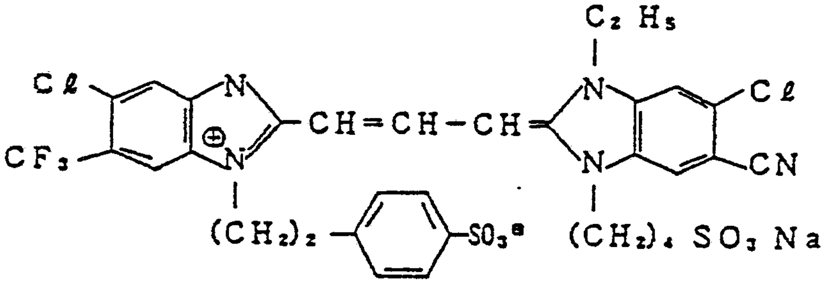
Sensitizing Dye VI



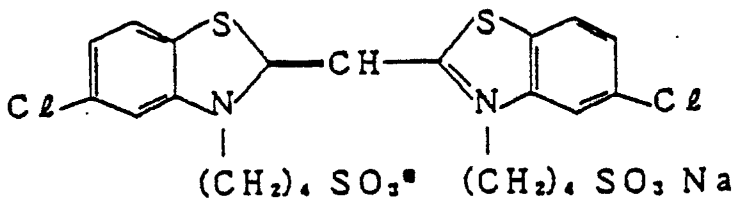
Sensitizing Dye VII



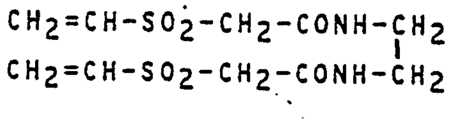
Sensitizing Dye VIII



Sensitizing Dye IX

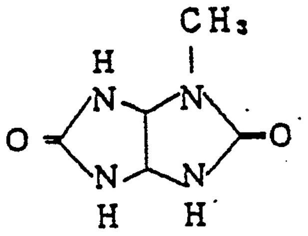


H-1

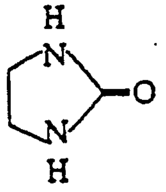


$$\begin{array}{l} CH_2=CH-SO_2-CH_2-CONH-CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2=CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

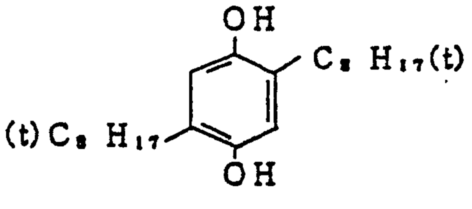
S-1



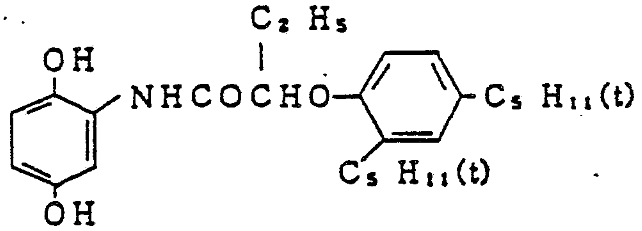
S-2



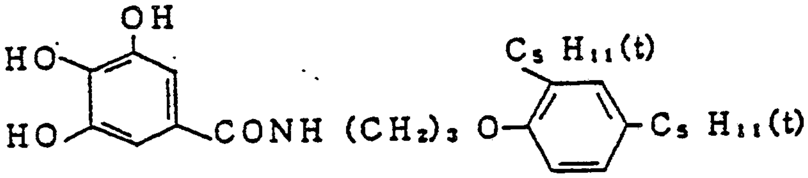
B-1 (Compound (6) of U.S. Patent No. 2,336,327)



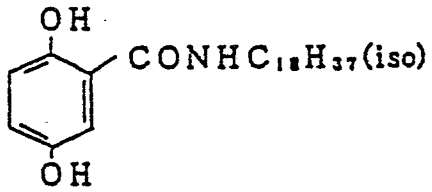
B-2 (Compound (3) of U.S. Patent No. 4,198,239)



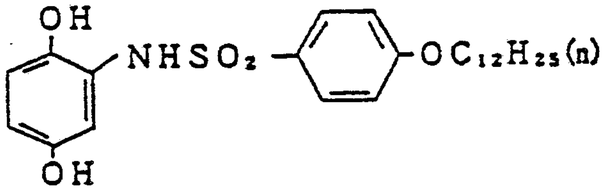
B-3 (Compound (11) of Japanese Patent Application (OPI) No. 156,933/83



B-4 (Compound (15) of Japanese Patent Application (OPI) No. 22,237/82



B-5 (Compound (3) of Japanese Patent Application (OPI) No. 202,465/84



Preparation of Samples 102 to 106

Samples 102 to 106 were prepared by replacing the Compound Cpd-A (Compound (9) of U.S. Patent 2,701,197) in the sixth layer of Sample 101 with equimolar amounts of the Comparative Compounds B-1 to B-5, respectively.

Preparation of Samples 107 to 111

Samples 107 to 111 were prepared by replacing the Compound Cpd-A in the sixth layer of Sample 101 with equimolar amounts of the compounds A-2, A-3, A-7, A-11 and A-26 of this invention.

Samples 101 to 111 were subjected to a red image exposure and color processed in the way described below. After processing the density of the samples was measured using a red filter and a green filter and the color turbidity, the value obtained by subtracting the magenta fog density from the magenta density at an exposure at which the cyan density measured with a red filter was (fog + 1.5), was as shown in Table 1.

The development process was carried out as follows.

Color Development	3 min. 15 sec. 38°C
Bleach	1 min. 38°C
Bleach-Fix	3 min. 15 sec. 38°C
Rinse	1 min. 40 sec. 38°C
Stabilization	40 sec. 38°C

The compositions of the processing baths used in each process were as follows:

Color Developer Bath

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

Bleach Bath

Ammonium Bromide	100 g
Ethylenediamine Tetra-acetic Acid Iron (III) Ammonium Salt	120 g
Ethylenediamine Tetra-acetic Acid di-sodium salt	10.0 g
Ammonium Nitrate	10.0 g
Bleach Accelerator (B-6)	2.0 g
Aqueous Ammonia	17.0 ml
Water to make	1 liter
pH	6.5

B-6: $[(CH_3)_2NCH_2CH_2S\,)]_2 \cdot 2HCl$

Bleach-Fix Bath

Ammonium Bromide	50.0 g
Ethylenediamine Tetra-acetic Acid iron (III) Ammonium Salt	50.0 g
Ethylenediamine Tetra-acetic Acid Disodium Salt	5.0 g
Ammonium Nitrate	5.0 g
Sodium Sulfite	12.0 g
Ammonium Thiosulfate, Aqueous Soln (70%)	240 ml
Aqueous Ammonia	10.0 ml
Water to make	1 liter
pH	7.3

Rinse Bath Ethylenediamine Tetra-acetic Acid Disodium Salt 0.4 g
Water to make 1 liter
Sodium Hydroxide was used to adjust to pH 7.0

Stabilizer Bath Formaldehyde (40% aq. soln) 2.0 ml
Polyoxyethylene-p-mono-nonylphenyl Ether (average degree of polymerization about 10) 0.3 g
Water to make 1.0 liter

Table 1

Sample	Compound	Color Turbidity
101 (Comparative Example)	Cpd-A	0.09
102 (")	B-1	0.17
103 (")	B-2	0.11
104 (")	B-3	0.07
105 (")	B-4	0.14
106 (")	B-5	0.12
107 (This Invention)	A-2	0.04
108 (")	A-3	0.05
109 (")	A-7	0.05
110 (")	A-11	0.03
111 (")	A-26	0.06

It is clear from Table 1 that there was little color turbidity with Samples 107 to 111 of this invention and that the compounds used in these samples have a high anti-color staining performance. The lower the turbidity value, the higher the anti-color staining performance.

EXAMPLE 2

Sample 201 was prepared by coating photosensitive layers of which the compositions were as indicated below to form a multi-layer structure on a cellulose triacetate film on which an undercoating layer had been established.

Preparation of Sample 201

In the case of silver halide and colloidal silver the amount coated is expressed in terms of grams of silver per square meter, in the case of couplers, additives and gelatin the amount coated is expressed in terms of grams per square meter and the amounts of the sensitizing dyes used are expressed in terms of the number of mols per mol of silver halide in the same layer. In the case of solvent the amount coated is expressed in terms of cc/m^2.

First Layer (Anti-halation Layer)Black Colloidal Silver 0.2

Gelatin	1.3
ExM-9	0.06
UV-4	0.03
UV-5	0.06
UV-3	0.06
Solv-1	0.15
Solv-2	0.15
Solv-3	0.05

Second Layer (Intermediate Layer)Gelatin 1.0

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

Third Layer Low Speed Red-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (AgI 4 mol%, Uniform AgI type, Projected sphere diameter 0.5 μ, Coefficient of variation of the projected sphere diameter 20%, plate like grains, diameter/thickness ratio = 3.0) Coated silver weight 1.2

Silver Iodobromide Emulsion (AgI 3 mol%, Uniform AgI type, Projected sphere diameter 0.3 μ, Coefficient of variation of the projected sphere diameter 15%, Spherical grains, diameter/thickness ratio = 1.0) Coated silver weight 0.6

Gelatin	1.0
ExS-1	4×10^{-4}
ExS-2	5×10^{-5}
ExC-1	0.05
ExC-2	0.50
ExC-3	0.03
ExC-4	0.12
ExC-5	0.01

Fourth Layer (High Speed Blue-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (AgI 6 mol%, Core-shell ratio 1:1 type with a high AgI core, Projected sphere diameter 0.7 μ, Coefficient of variation of the projected sphere diameter 15%, Tabular grains, diameter/thickness ratio = 5.0) Coated silver weight 0.7

Gelatin	1.0
ExS-1	3×10^{-4}
ExS-2	2.3×10^{-5}
ExC-6	0.11
ExC-7	0.05
ExC-4	0.05
Solv-1	0.05
Solv-3	0.05

Fifth Layer (Intermediate Layer)Gelatin 0.5

Cpd-1	0.1
Solv-1	0.05

Sixth Layer (Low Speed Green-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (AgI 4 mol%, Core-shell ratio 1:1 type with a high AgI core, Projected sphere diameter 0.5 μ, Coefficient of variation of the projected sphere diameter 15%, Plate like grains, diameter/thickness ratio = 4.0) Coated silver weight 0.35

Silver Iodobromide Emulsion (AgI 3 mol%, Uniform AgI type, Projected sphere diameter 0.3 μ, Coefficient of variation of the projected sphere diameter 25%, Spherical grains, diameter/thickness ratio = 1.0) Coated silver weight 0.20

Gelatin	1.0
ExS-3	5×10^{-4}
ExS-4	3×10^{-5}
ExS-5	1×10^{-4}
ExM-8	0.4
ExM-9	0.07
ExM-10	0.02
ExY-11	0.03
Solv-1	0.3
Solv-4	0.05

Seventh Layer (High Speed Green-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (AgI 4 mol%, Core-shell ratio 1:3 type with a high AgI core, Projected sphere diameter 0.7 μ, Coefficient of variation of the projected sphere diameter 20%, Plate like grains, diameter/thickness ratio = 5.0) Coated silver weight 0.8

Gelatin	0.5
ExS-3	5×10^{-4}
ExS-4	3×10^{-4}
ExS-5	1×10^{-4}
ExM-8	0.1
ExM-9	0.02
ExY-11	0.03
ExC-2	0.03
ExM-14	0.01
Solv-1	0.2
Solv-4	0.01

Eighth Layer (Intermediate Layer)Gelatin 0.5

Cpd-1	0.05
Solv-1	0.02

Ninth Layer (Interlayer Effect Toner Layer for the Red-Sensitive Layer)Silver Iodobromide Emulsion (AgI 2 mol%, Core-shell ratio 2:1 type with a high AgI core, Projected sphere diameter 1.0 μ, Coefficient of variation of the projected sphere diameter 15%, Plate like grains, diameter/thickness ratio = 6.0) Coated silver weight 0.35

Silver Iodobromide Emulsion (AgI 2 mol%, Core-shell ratio 1:1 type with a high AgI core, Projected sphere diameter 0.4 μ, Coefficient of variation of the projected sphere diameter 20%, Plate like grains, diameter/thickness ratio = 6.0) Coated silver weight 0.20

Gelatin	0.5
ExS-3	8×10^{-4}
ExY-13	0.11

ExM-12	0.03
ExM-14	0.10
Solv-1	0.20

Tenth Layer (Yellow Filter Layer)Yellow Colloidal Silver 0.05

Gelatin	0.5
Cpd-2	0.13
Cpd-1	0.10

Eleventh Layer (Low Speed Blue-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (AgI 4.5 mol%, Uniform AgI type, Projected sphere diameter 0.7 μ, Coefficient of variation of the projected sphere diameter 15%, Plate like grains, diameter/thickness ratio = 7.0) Coated silver weight 0.3

Silver Iodobromide Emulsion (AgI 3 mol%, Uniform AgI type, Projected sphere diameter 0.3 μ, Coefficient of variation of the projected sphere diameter 25%, Plate like grains, diameter/thickness ratio = 7.0) Coated silver weight 0.15

Gelatin	1.6
ExS-6	2×10^{-4}
ExC-16	0.05
ExC-2	0.10
ExC-3	0.02
ExY-13	0.07
ExY-15	1.0
ExC-17	0.3
Solv-1	0.20

Twelfth Layer (High Speed Blue-Sensitive Emulsion Layer)Silver Iodobromide Emulsion (AgI 10 mol%, High internal AgI type, Projected sphere diameter 1.0 μ, Coefficient of variation of the projected sphere diameter 25%, Multiple twined crystal plate like grains, diameter/thickness ratio = 2.0) Coated silver weight 0.5

Gelatin	0.5
ExS-6	1×10^{-4}
ExY-15	0.20
ExY-13	0.01
Solv-1	0.10

Thirteenth Layer (First Protective Layer)Gelatin 0.8

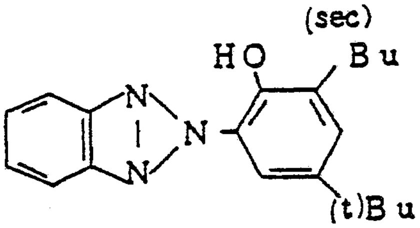
UV-1	0.1
UV-2	0.15
Solv-1	0.01
Solv-2	0.01

Fourteenth Layer (Second Protective Layer)Fine Grained Silver Indobromide Emulsion (AgI 2 mol%, Uniform AgI type, Projected sphere diameter 0.07 μ) 0.5

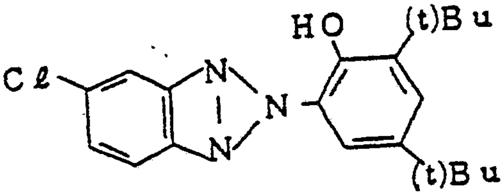
Gelatin	0.45
Poly(methyl methacrylate) Grains, average diameter 1.5 μ	0.2
H-1	0.4
Cpd-5	0.5
Cpd-6	0.5

Emulsion stabilizer Cpd-3 (0.04 g per square meter) and surfactant Cpd-4 (0.02 g per square meter) were added as coating promotors to each layer as well as the components indicated above.

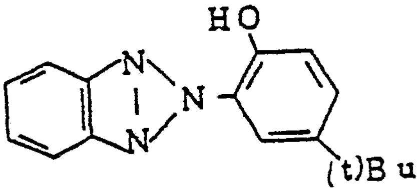
UV-3



UV-4



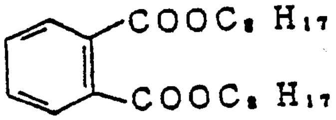
UV-5



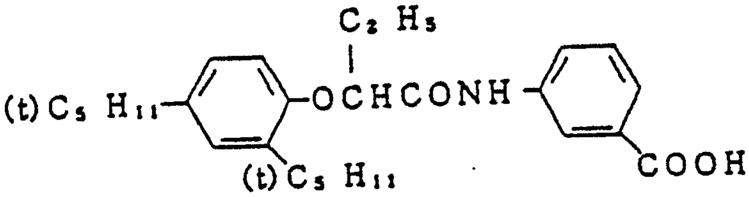
Solv-1 Tricresyl phosphate

Solv-2 Dibutyl phthalate

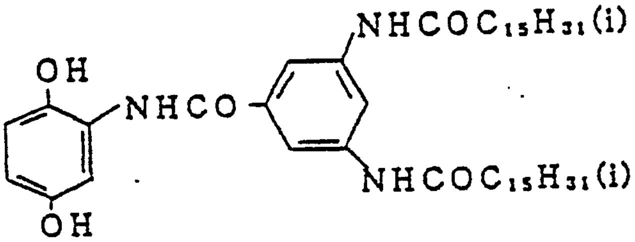
Solv-3



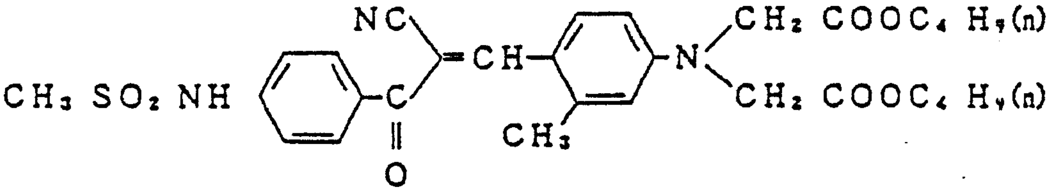
Solv-4



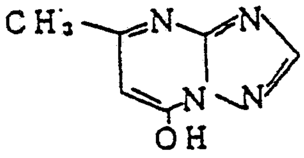
Cpd-1



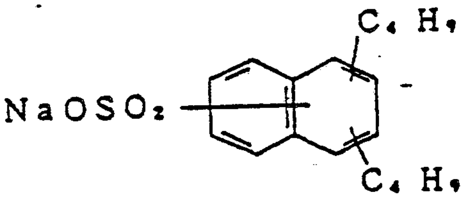
Cpd-2



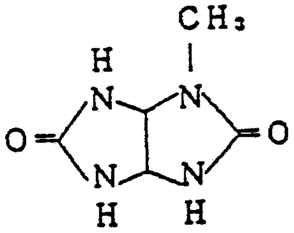
Cpd-3



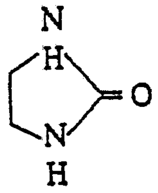
Cpd-4



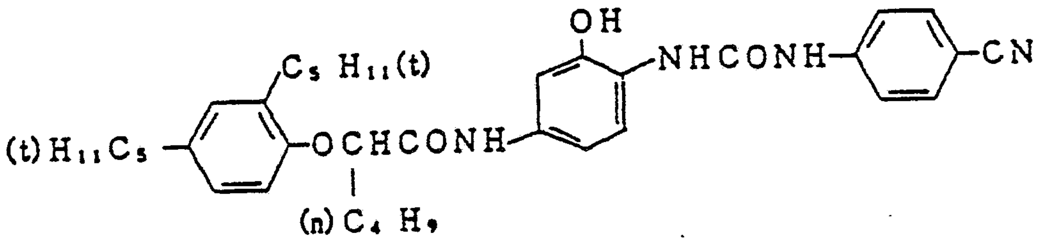
Cpd-5



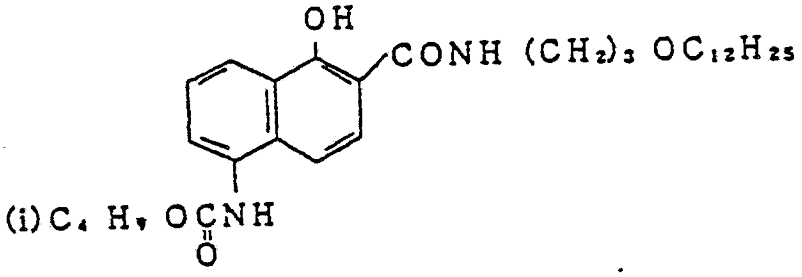
Cpd-6



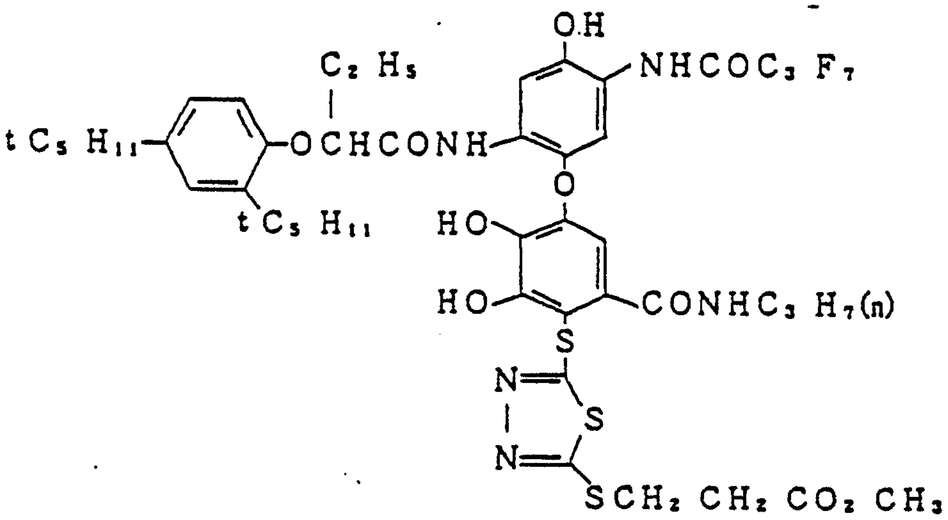
ExC-1



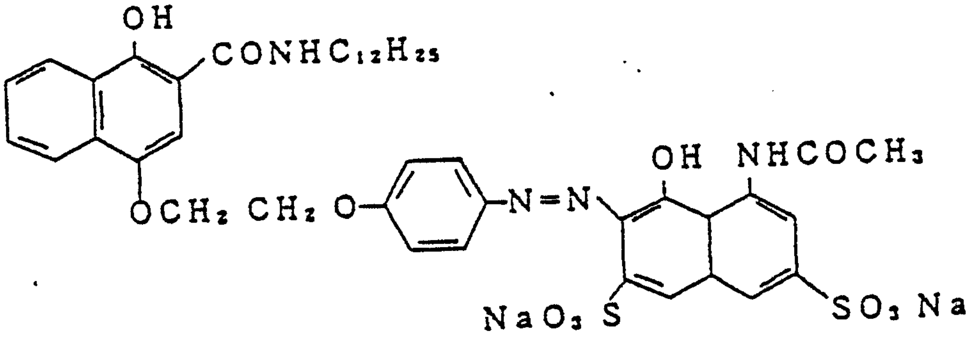
ExC-2



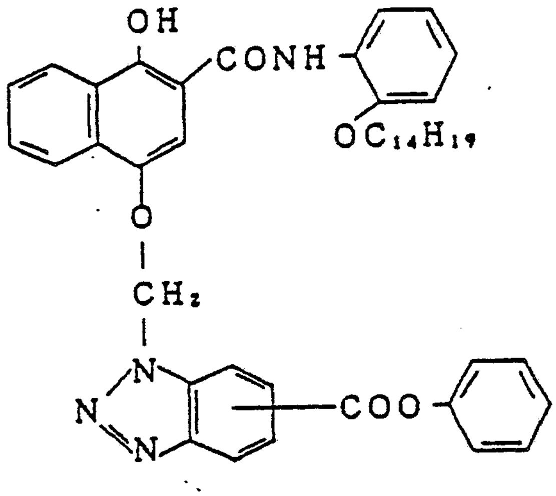
ExC-3



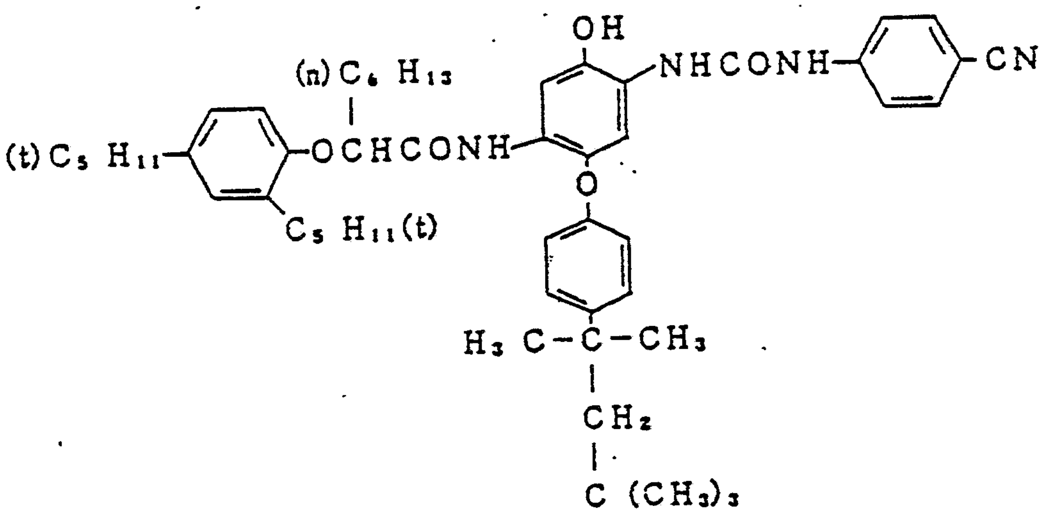
ExC-4



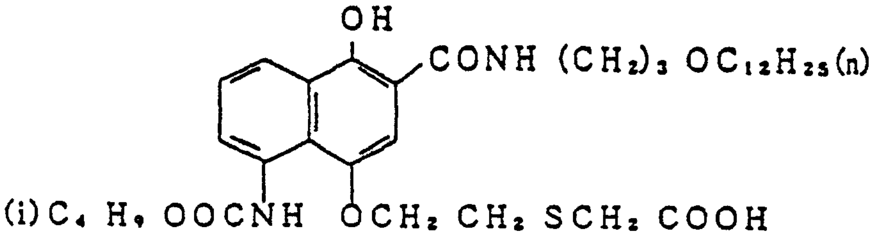
ExC-5


OH
CONH
OC14H19
O
CH2
N
N
N
COO

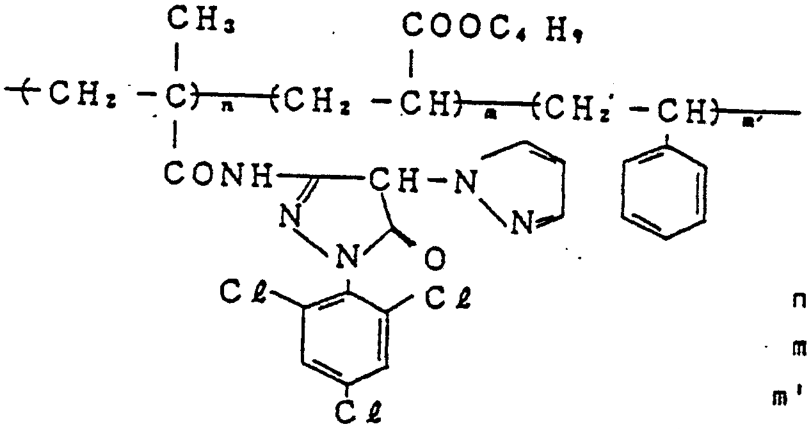
ExC-6


OH
NHCONH
CN
(n)C6 H13
(t)C5 H11
OCHCONH
C5 H11(t)
O
H3 C-C-CH3
CH2
C (CH3)3

ExC-7

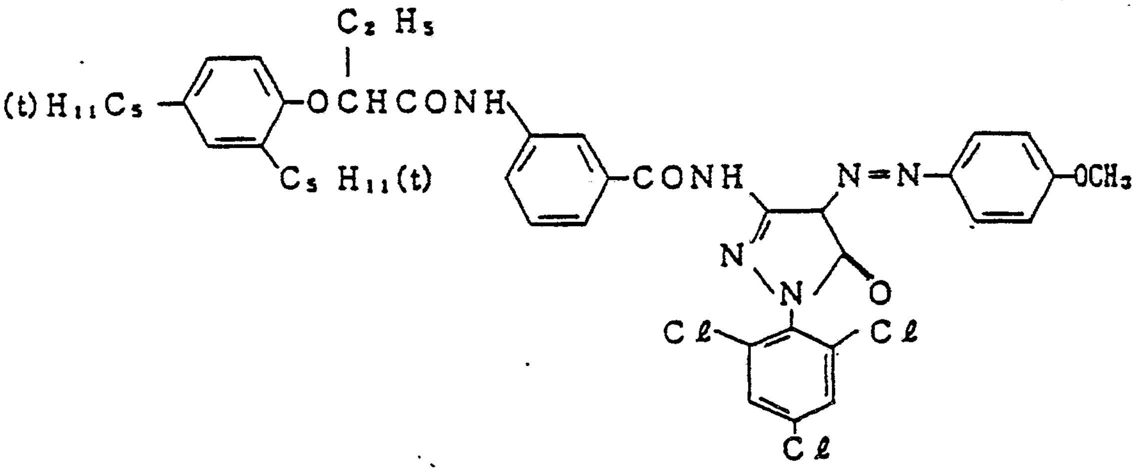


ExM-8



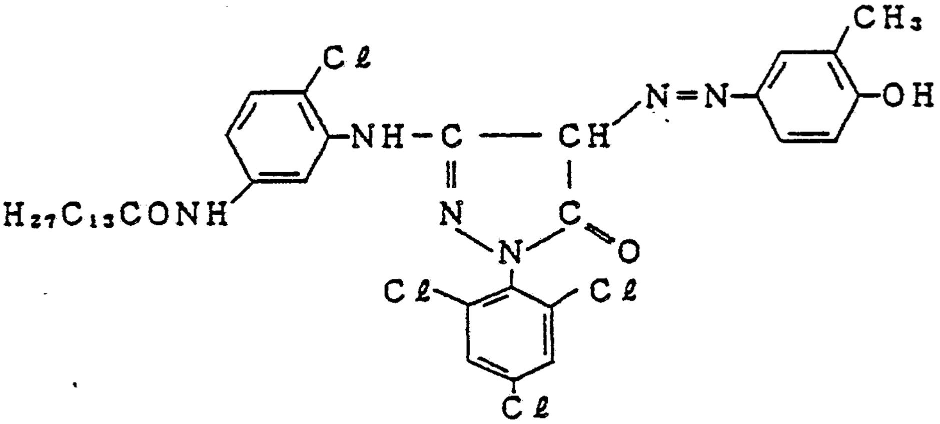
n = 50
m = 25
m' = 25
mol.wt. about 20,000

ExM-9



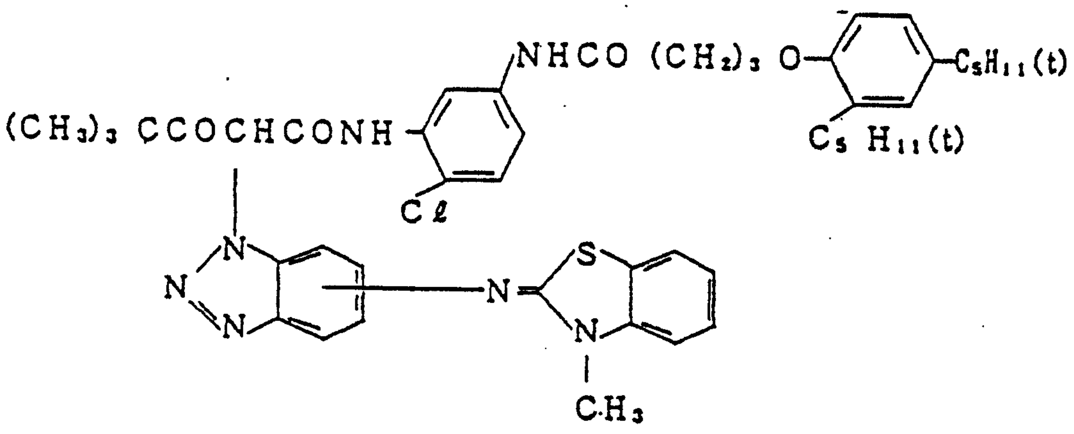
C_2H_5
$(t)H_{11}C_5$
OCHCONH
$C_5H_{11}(t)$
CONH
N=N
OCH_3
N
N
O
Cℓ
Cℓ
Cℓ

ExM-10



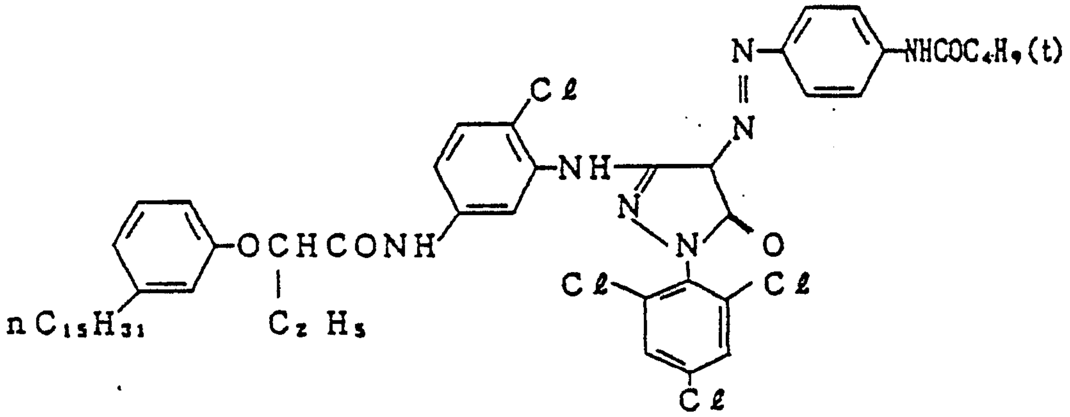
CH_3
Cℓ
NH–C
CH
N=N
OH
$H_{27}C_{13}CONH$
N
C
O
N
Cℓ
Cℓ
Cℓ

ExM-11



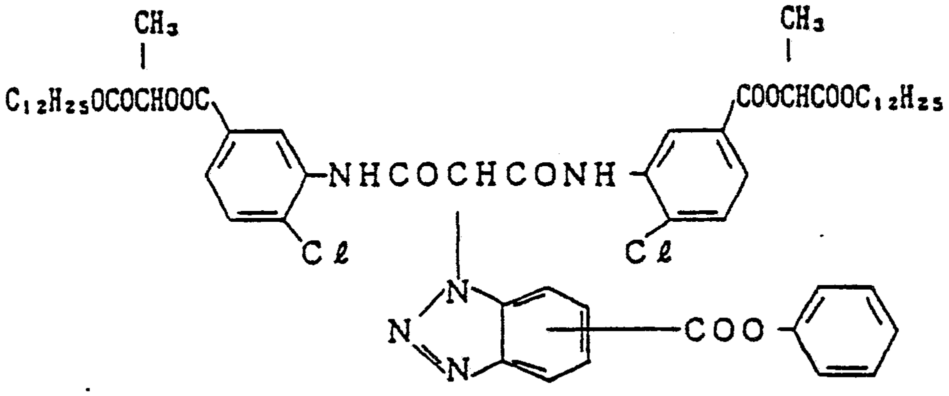
NHCO (CH₂)₃ O
C₅H₁₁(t)
C₅ H₁₁(t)
(CH₃)₃ CCOCHCONH
Cℓ
N
N
N
N
S
N
CH₃

ExM-12

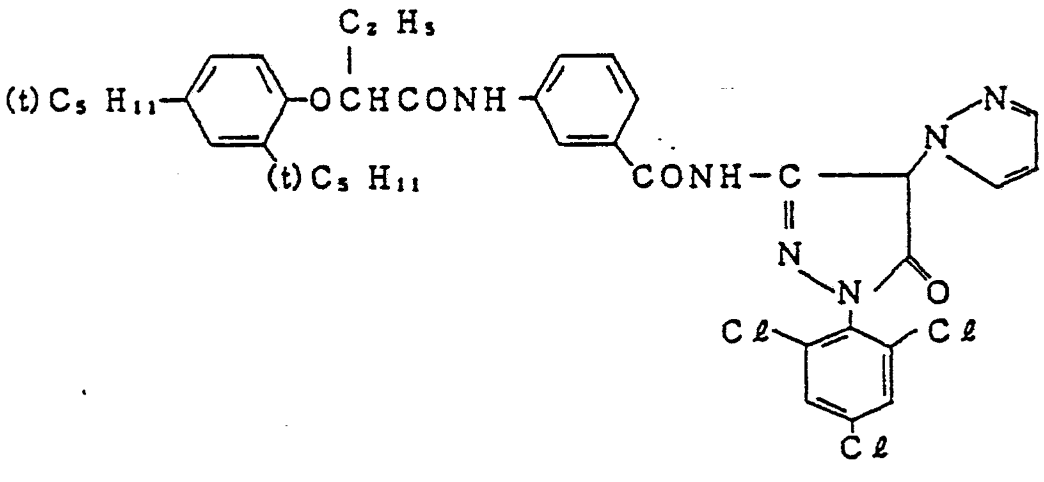


N
N
NHCOC₄H₉(t)
Cℓ
NH
N
N
O
OCHCONH
C₂ H₅
nC₁₅H₃₁
Cℓ
Cℓ
Cℓ

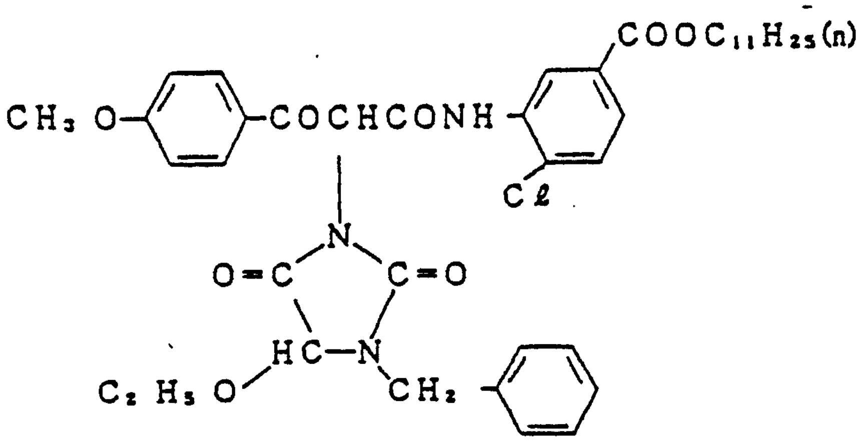
ExY-13


CH₃
C₁₂H₂₅OCOCHOOC
NHCOCHCONH
Cl
CH₃
COOCHCOOC₁₂H₂₅
Cl
N
N
N
COO

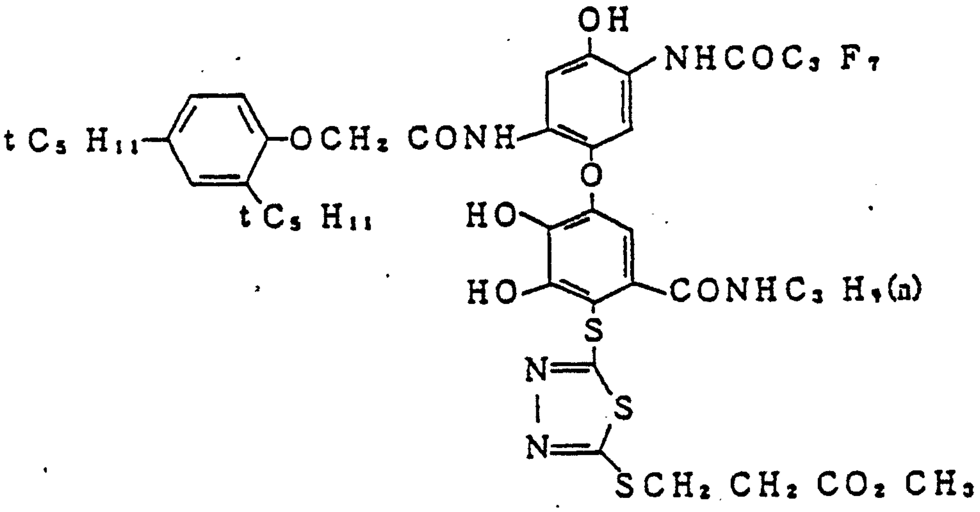
ExM-14


C₂H₅
(t)C₅H₁₁
OCHCONH
(t)C₅H₁₁
CONH
C
N
N
O
N
N
Cl
Cl
Cl

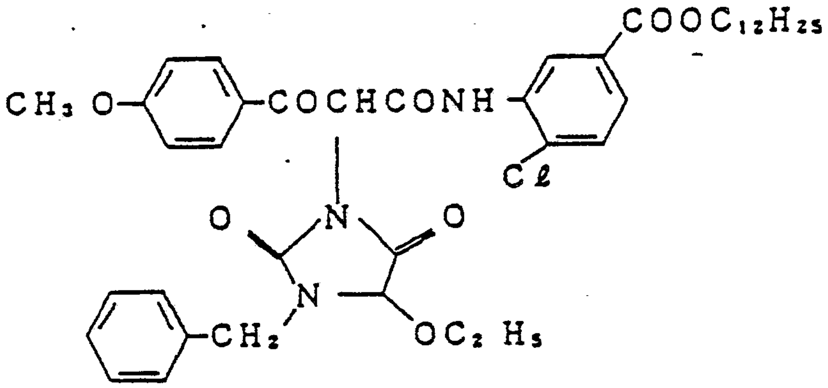
ExY-15


CH₃ O
COCHCONH
COOC₁₁H₂₅(n)
Cℓ
N
O=C
C=O
HC—N
C₂ H₅ O
CH₂

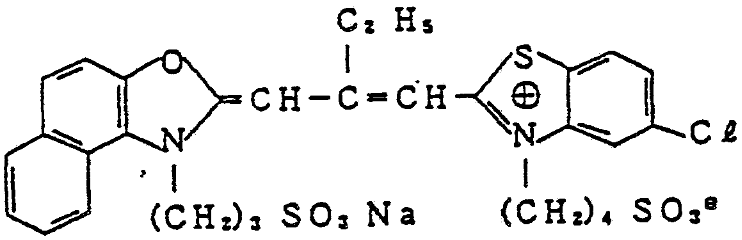
ExC-16


OH
NHCOC₃ F₇
tC₅ H₁₁
OCH₂ CONH
O
tC₅ H₁₁
HO
HO
CONHC₃ H₉(n)
S
N
S
N
SCH₂ CH₂ CO₂ CH₃

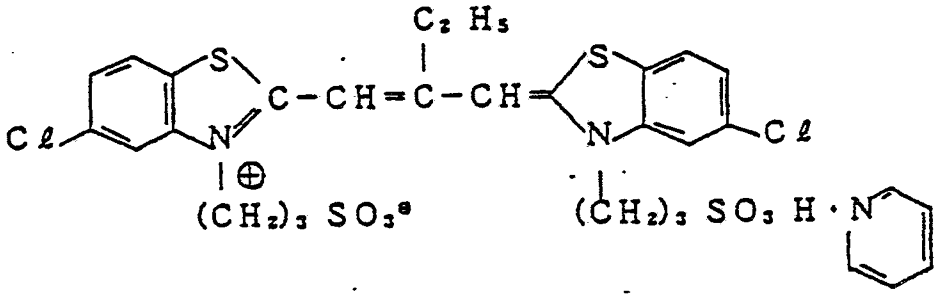
ExY-17



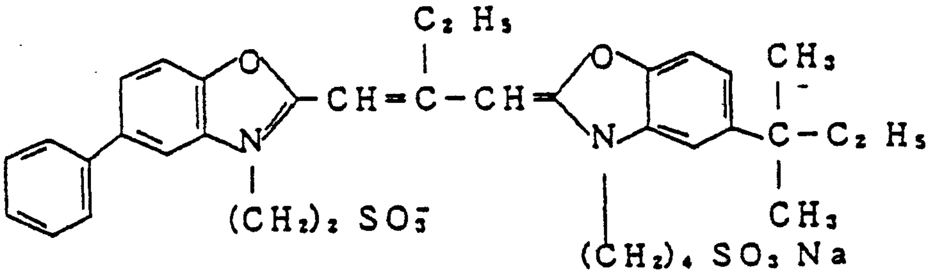
ExS-1



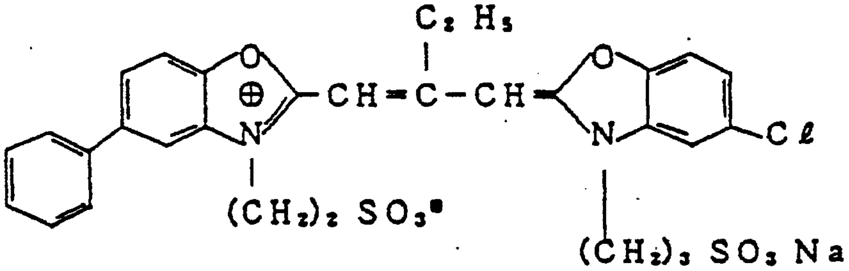
ExS-2



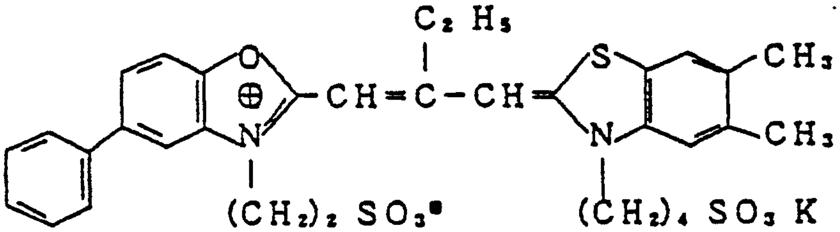
ExS-3



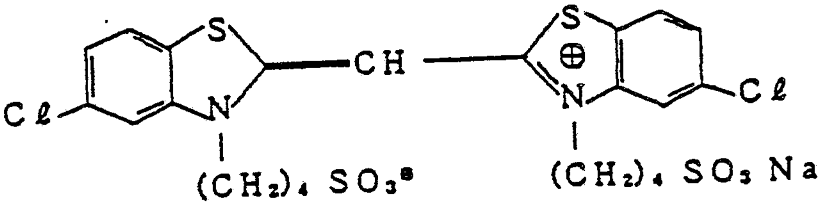
ExS-4



ExS-5



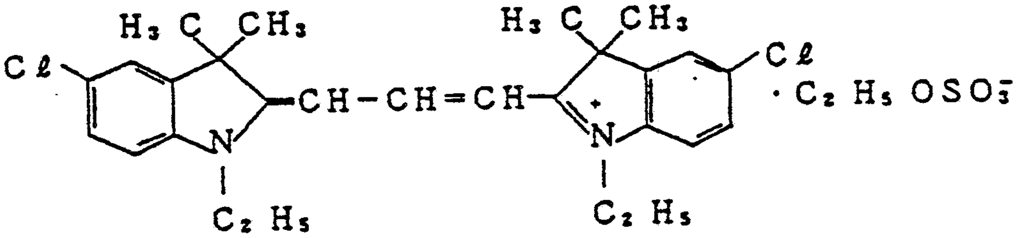
ExS-6



H-1

$CH_2=CH-SO_2-CH_2-CONH-CH_2$

ExF-1



<u>Preparation of Samples 202 to 206</u>

Samples 202 to 206 were prepared by replacing compound Cpd-1 in the fifth layer of Sample 201 with equimolar amounts of the comparative compound B-1 to B-5, respectively.

<u>Preparation of Sample 207</u>

Sample 207 was prepared by replacing compound Cpd-1 in the fifth layer of Sample 201 with Cpd-A, which was used as a comparative compound in Sample 101 of Example 1.

Preparation of Samples 208 to 212

Samples 208 to 212 were prepared by replacing compound Cpd-1 in the fifth layer of Sample 201 with equimolar amounts of the compounds A-1, A-3, A-5, A-7 and A-27 according to this invention, respectively.

Test 1

The above mentioned Samples 201 to 210 were subjected to a red image exposure and a color development process as indicated below. The density of the processed samples was measured with a red filter and a green filter and the color turbidity, a value obtained by subtracting the magenta fog density from the magenta density at an exposure at which the cyan density measured with the red filter was (fog + 1.5), was as shown in column I in Table 2.

The color development process used here was that described as color development process A below.

Color Development Process A

Process	Processing Time	Processing Temperature
Color Development	2 min. 30 sec.	40°C
Bleach-fix	3 min. 00 sec.	40°C
Wash (1)	20 sec.	35°C
Wash (2)	20 sec.	35°C
Stabilization	20 sec.	35°C
Drying	50 sec.	65°C

The compositions of the processing baths were as follows:

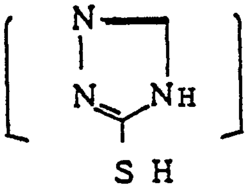
Color Developer Bath

(Units: Grams)

Diethylenetriamine Penta-acetic Acid	2.0
1-Hydroxyethylidene-1,1-diphosphonic Acid	3.0
Sodium Sulfite	4.0
Potassium Carbonate	30.0
Potassium Bromide	1.4
Potassium Iodide	1.5 (mg)
Hydroxylamine Sulfate	2.4
4-[N-ethyl-N-(β-hydroxyethyl)amino]-2-methylaniline Sulfate	4.5
Water to make up to	1.0 liter
pH	10.5

Bleach-Fix Bath

	(Units: Grams)
Ethylenediamine Tetra-acetic Acid Iron (III) Ammonium Salt Dihydrate	50.0
Ethylenediamine Tetra-acetic Acid Di-sodium Salt	5.0
Sodium Sulfite	12.0
Ammonium Thiosulfate (aq. soln 70%)	260.0 ml
Acetic Acid (98%)	5.0 ml
Bleach accelerator	0.01 mol



Water to make	1 liter
pH	6.0

Water Wash

Town water was treated by passage through a mixed bed type column packed with an H-type strongly acidic cation exchange resin ("Amberlite IR-120B", made by the Rohm and Haas Co.) and an OH-type anion exchange resin ("Amberlite IR-400", made by the same company), the calcium and magnesium ion contents being reduced to less than 3 mg/liter, after which 20 mg/liter of sodium dichloroisocyanurate and 1.5 g/liter of sodium sulfate were added.

The pH of this liquid was within the range 6.5 to 7.5.

Stabilizer Bath

	(Units: Grams)
Formaldehyde (37%)	2.0 ml
Polyoxyethylene-p-mono-nonylphenyl ether (average degree of polymerization 10)	0.3
Ethylenediamine tetra-acetic acid Di-Sodium Salt	0.05
Water to make	1.0 liter
	pH 5.8 - 8.0

Furthermore, similar results to those shown in Table 2 were obtained when the color development process B indicated below was used in place of the color development process A.

Color Development Process B

Processing was carried out in an automatic developing machine using the method indicated below until the total amount of replenishment of the color developer bath reached 3 times the original bath tank capacity.

Process	Processing Time	Processing Temperature	Replenishment Rate	Time Capacity
Color Development	2 min. 30 sec.	40°C	10 ml	8 liters
Bleach-fix	3 min. 00 sec.	40°C	20 ml	8 liters
Wash (1)	20 sec.	35°C	Counter-flow pipe system (2) + (1)	2 liters
Wash (2)	20 sec.	35°C	10 ml	2 liters
Stabilization	20 sec.	35°C	10 ml	2 liters
Drying	50 sec.	65°C		

Replenishing rates per 1 m x 35 mm wide.

The compositions of the processing baths were as follows:

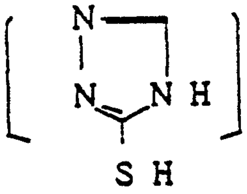
Color Developer Bath

	Original Bath (g)	Replenisher (g)
Diethylenetriamine Penta-acetic Acid	2.0	2.2
1-Hydroxyethylidene-1,1-Diphosphonic Acid	3.0	3.2
Sodium Sulfite	4.0	5.5
Potassium Carbonate	30.0	45.0
Potassium Bromide	1.4	-
Potassium Iodide	1.5 (mg)	-
Hydroxylamine Sulfate	2.4	3.0
4-[N-ethyl-N-(β-hydroxyethyl)amino]-2-methylaniline Sulfate	4.5	7.5
Water to make	1.0 ℓ	1.0 ℓ
pH	10.5	10.20

Bleach-Fix Bath (Original bath and replenisher are the same)

	(Units: grams)
Ethylenediamine Tetra-acetic Acid Iron (III) Ammonium Salt Dihydrate	50.0
Ethylenediamine Tetra-acetic Acid Di-Sodium Salt	5.0
Sodium Sulfite	12.0
Ammonium Thiosulfate (aq. soln 70%)	260.0 ml
Acetic Acid (98%)	5.0 ml

Bleach Accelerator		0.01 mol



Water to make		1 liter
	pH	6.0

Water Wash (Original bath and replenisher were the same)

Town water was treated by passage through a mixed bed type column packed with an H-type strongly acidic cation exchange resin ("Amberlite IR-120B", made by the Rohm and Haas Co.) and an OH-type anion exchange resin ("Amberlite IR-400", made by the same company), the calcium and magnesium ion contents being reduced to less than 3 mg/liter, after which 20 mg/liter of sodium dichloroisocyanurate and 1.5 g/liter of sodium sulfate were added.

The pH of this liquid was within the range 6.5 to 7.5.

Stabilizer Bath (Original bath and replenisher were the same)

	(Units: Grams)
Formaldehyde (aq. soln 37%)	2.0 ml
Polyoxyethylene-p-mono-nonylphenyl ether (average degree of polymerization 10)	0.3
Ethylenediamine tetra-acetic acid Di-Sodium Salt	0.05
Water to make	1.0 liter
pH	5.8 - 8.0

Furthermore, these samples were left to stand for 7 days under conditions of (A) 25°C, 60% relative humidity and (B) 40°C, 80% relative humidity and then subjected to a white light image exposure and the aforementioned color processing. The magenta and cyan densities at an exposure (E_y) such that the yellow density was 1.5 were taken to be D_m and D_c respectively under conditions A. The yellow, magenta and cyan densities under the enforced deterioration conditions (B) for an exposure E_y were taken as D_y', D_m' and D_c' and the differences ($1.5-D_y'$, D_m-D_m', D_c-D_c') were as shown in column (II) in Table 2.

Table 2

Sample	Compound	I Color Turbidity	II $1.5\text{-}D_y{}'$	 $D_m\text{-}D_m{}'$	 $D_c\text{-}D_c{}'$
201 (Comparative Example)	Cpd-1	0.08	0.00	0.03	0.05
202 (")	B-1	0.16	0.00	0.04	0.08
203 (")	B-2	0.13	0.01	0.01	0.06
204 (")	B-3	0.06	-0.01	0.09	0.16
205 (")	B-4	0.11	0.01	0.05	0.14
206 (")	B-5	0.14	0.00	0.06	0.13
207 (")	Cpd-A	0.09	0.03	0.10	0.17
208 (The Invention)	A-1	0.03	0.00	0.03	0.04
209 (")	A-2	0.05	0.00	0.01	0.03
210 (")	A-3	0.04	-0.01	0.01	0.04
211 (")	A-4	0.05	0.00	0.01	0.03
212 (")	A-5	0.06	0.01	0.02	0.03

It is clear from Table 2 (Column I) that the color turbidity is low in the case of Samples 208 to 212 of this invention and Sample 204 and that the compounds used in these samples have a high anti-color staining performance.

Furthermore, it is clear from (Column II) that after standing under the enforced deterioration conditions the magenta and cyan densities of Samples 201 to 207 fell considerably when compared to the falls recorded with Samples 208 to 212 of this invention. There was a remarkable reduction in the densities with Samples 204 to 207.

The effectiveness of the invention is therefore clear.

EXAMPLE 3

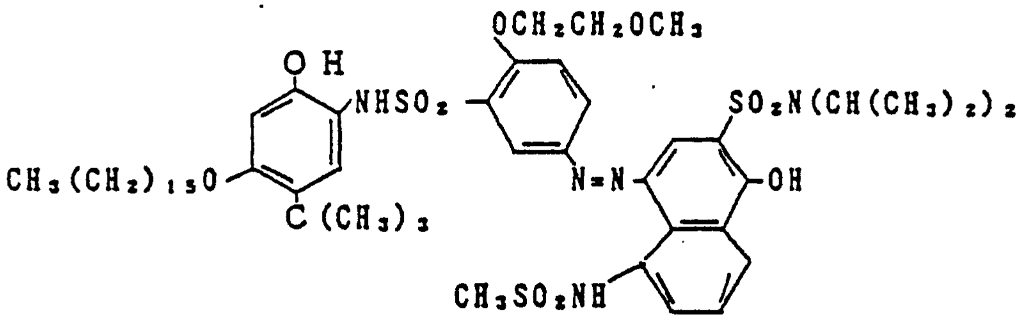
Photosensitive sheet A was prepared by coating the layers indicated below sequentially on a transparent poly(ethylene terephthalate) film.

(1) A mordant layer containing 3.0 g per square meter of co-poly(styrene-N-vinylbenzyl-N,N,N-trihexylammonium chloride) and 3.0 g per square meter of gelatin.

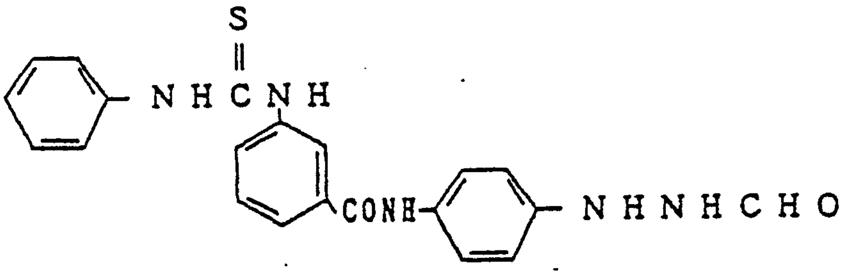
(2) A light reflecting layer containing 20 g per square meter of titanium dioxide and 2.0 g per square meter of gelatin.

(3) A light shielding layer containing 3.0 g per square meter of carbon black and 2.0 g per square meter of gelatin.

(4) A layer containing 0.65 g per square meter of the magenta dye releasing redox compound of which the structure is indicated below and 1.2 g per square meter of gelatin.

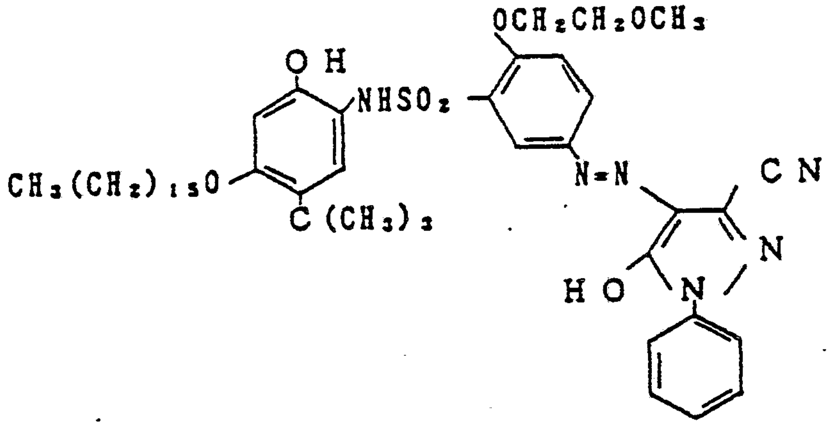


(5) A layer containing a green-sensitive internal latent image type direct reversal silver bromide emulsion (1.2 g as silver per square meter), gelatin (1.3 g per square meter), the nucleating agent of which the structure is indicated below (0.04 mg per square meter) and 2-sulfo-5-n-pentadecylhydroquinone sodium salt (0.12 g per square meter).



(6) A layer containing 0.5 g per square meter of compound A-1 of this invention and 0.2 g per square meter of tricyclohexylphosphate.

(7) A layer containing 0.75 g per square meter of the yellow dye releasing redox compound of which the structure is indicated below, 0.2 g per square meter of tricyclohexylphosphate and 1.2 g per square meter of gelatin.



(8) A layer containing gelatin (1.0 g per square meter).

Photosensitive Sheet B and Photosensitive Sheets C and D for comparative purposes were prepared in the same way with the following differences.

* Photosensitive Sheet B:

This was the same as photosensitive sheet A except that an equimolar amount of 2,5-di-tert-pentadecylhydroquinone as disclosed in Japanese Patent Application (OPI) No. 29637/79 was coated to a coverage of 0.35 g per square meter as an anti-color staining agent in place of the compound of this invention in layer 6 of the photosensitive sheet A.

* Photosensitive Sheet C:

This was the same as photosensitive sheet A except that the anti-color staining agent in layer 6 of the photosensitive sheet A was replaced by an equimolar amount of 2-sec-octadecyl-5-benzenesulfonyl-hydroquinone (compound (22) of U.S. Patent 4,277,553), coated at 0.29 g per square meter.

* Photosensitive Sheet D:

This was the same as photosensitive sheet A except that layers 7 and 8 of photosensitive sheet A were not coated.

A cover sheet was prepared by coating the layers indicated below sequentially on a transparent polyester support.

(1) A layer coated to a thickness of 7 microns which contained 17 g per square meter of poly(acrylic acid), 0.06 g per square meter of N-hydroxysuccinimidobenzenesulfonate and 0.5 g per square meter of ethylene glycol.

(2) A timing layer for which cellulose acetate (degree of acetylation 54) was coated to a thickness of 2 microns.

(3) A timing layer for which a vinylidene chloride-acrylic acid copolymer latex was coated to a thickness of 4 microns.

A development liquid of the composition indicated below was prepared.

1-Phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidone	13 g
Methylhydroquinone	0.3 g
5-Methylbenzotriazole	3.5 g
Sodium Sulfite (anhydrous)	0.2 g
Carboxymethylcellulose sodium salt	58 g
Potassium hydroxide (28% aq. soln)	200 cc

Benzyl alcohol	1.5 cc
Carbon black	150 g
Water	685.cc

The above described Photosensitive Sheets A to D were given a wedge exposure and then unified with a container which contained the aforementioned development liquid and cover sheet, and a transfer colored image was obtained by spreading the developer liquid to a thickness of 80 microns by means of pressure under conditions of 25°C and 35°C. The transfer image was subjected to measurement with a color densitometer and the values of D_g (green filter density) and D_b (blue filter density) were obtained. The value of $D_b$when D_g was 2.0 was as shown in Table 3.

Table 3

Photosensitive Sheet	Processing Temperature 35°C			Processing Temperature 25°C			Remarks
	D_g	D_b	Difference Between D_b and D_b of Photosensitive Sheet D	D_g	D_b	Difference Between D_b and D_b of Photosensitive Sheet D	
Photosensitive Sheet A	2.00	0.44	0.08	2.00	0.41	0.06	Compound of the Invention
Photosensitive Sheet B	2.00	0.79	0.43	2.00	0.63	0.28	For Comparative Purposes
Photosensitive Sheet C	2.00	0.72	0.36	2.00	0.58	0.23	For Comparative Purposes
Photosensitive Sheet D	2.00	0.36	-	2.00	0.35	-	Values when no color turbidity occurred

Layer 6, which contained the anti-color staining agents in the Photosensitive Sheets A to C prepared here, was provided in order to prevent reaction between the oxidized form of the developer and the release of the yellow dye when the oxidized form of the developer formed in layer 5, which contains the green sensitive silver halide emulsion, diffuses, passing through the layer 6 towards the layer 7, which contains a yellow dye releasing redox compound which is not connected with the silver halide emulsion layer 5 (this would not result in magenta color turbidity, which is to say that the layer 6 prevents the mixing of yellow with the magenta and prevents any deterioration of the magenta hue). Hence the performance of the layer 6 which contains the anti-color staining agent in the photosensitive sheets A, B and C can be assessed by means of the value of Db-Db (Photosensitive Sheet D), which is to say by the color turbidity. Photosensitive Sheet A, in which a compound of this invention was used, had a much lower color turbidity than the Photosensitive Sheets B and C prepared for comparison, thus it clearly demonstrated between anti-color staining performance.

EXAMPLE 4

Preparation of Sample 401

A multi-layer color photosensitive material consisting of each of the layers of which the compositions are indicated below on an undercoated cellulose triacetate film support was prepared as Sample 401.

First Layer (Anti-halation Layer)

A gelatin layer (dry film thickness 2 μ) containing: Black Colloidal Silver 0.25 g/m^2
Ultraviolet Absorber U-1 0.04 g/m^2
Ultraviolet Absorber U-2 0.1 g/m^2
Ultraviolet Absorber U-3 0.1 g/m^2
High Boiling Point Organic Solvent Oil-2 0.01 cc/m^2

Second Layer (Intermediate Layer)

A gelatin layer (dry film thickness 1 μ) containing: Compound Cpd-C 0.05 g/m^2
Compound I-1 0.05 g/m^2
High Boiling Point Organic Solvent Oil-1 0.05 cc/m^2

Third Layer (First Red-Sensitive Emulsion Layer)

A gelatin layer (dry film thickness 1 μ) containing: Silver bromide emulsion which had been spectrally sensitized with the sensitizing dyes S-1 and S-2 (average grain size 0.3 μ, AgI content 4 mol%) 0.5 g/m^2 as silver
Coupler F-1 0.2 g/m^2
Coupler F-2 0.05 g/m^2
Compound I-2 2×10^{-3} g/m^2
High Boiling Point Organic Solvent Oil-1 0.12 cc/m^2

Fourth Layer (Second Red-Sensitive Emulsion Layer)

A gelatin layer (dry film thickness 2.5 μ) containing: Silver bromide emulsion which had been spectrally sensitized with the sensitizing dyes S-1 and S-2 (average grain size 0.6 μ, AgI content 3 mol%) 0.8 g/m^2 as silver

Coupler F-1 0.55 g/m^2
Coupler C-2 0.14 g/m^2
Compound I-2 1×10^{-3} g/m^2
High Boiling Point Organic Solvent Oil-1 0.33 cc/m^2
Dye D-I 0.02 g/m^2

Fifth Layer (Intermediate Layer)

A gelatin layer (dry film thickness 1 μ) containing: Compound Cpd-C 0.1 g/m^2
High Boiling Point Organic Solvent Oil-1 0.1 cc/m^2
Dye D-2 0.02 g/m^2

Sixth Layer (First Green-Sensitive Emulsion Layer)

A gelatin layer (dry film thickness 1 μ) containing: Silver iodobromide emulsion containing the sensitized dyes S-3 and S-4 (average grain size 0.3 μ, AgI content 4 mol%) 0.7 g/m^2 as silver
Coupler F-3 0.20 g/m^2
Coupler F-5 0.10 g/m^2
High Boiling Point Organic Solvent Oil-1 0.26 cc/m^2

Seventh Layer (Second Green-Sensitive Emulsion Layer)

A gelatin layer (dry film thickness 2.5 μ) containing: Silver iodobromide emulsion containing the sensitized dyes S-3 and S-4 (average grain size 0.6 μ, AgI content 2.5 mol%) 0.7 g/m^2 as silver
Coupler F-4 0.10 g/m^2
Coupler F-5 0.10 g/m^2
High Boiling Point Organic Solvent Oil-1 0.05 cc/m^2
Dye D-3 0.05 g/m^2

Eighth Layer (Intermediate Layer)

A gelatin layer (dry film thickness 1 μ) containing: Compound Cpd-C 0.05 g/m^2
High Boiling Point Organic Solvent Oil-2 0.1 cc/m^2
Dye D-4 0.01 g/m^2

Ninth Layer (Yellow Filter Layer)

A gelatin layer (dry film thickness 1 μ) containing: Yellow Colloidal Silver 0.1 g/m^2
Compound Cpd-C 0.02 g/m^2
High Boiling Point Organic Solvent Oil-1 0.04 cc/m^2

Tenth Layer (First Blue-Sensitive Emulsion Layer)

A gelatin layer (dry film thickness 1.5 μ) containing: Silver iodobromide emulsion containing the sensitized dye S-5 (average grain size 0.3 μ, AgI content 2 mol%) 0.6 g/m² as silver

Coupler F-6	0.1 g/m²
Coupler F-7	0.4 g/m²
High Boiling Point Organic Solvent Oil-1	0.1 cc/m²

Eleventh Layer (Second Blue-Sensitive Emulsion Layer)

A gelatin layer (dry film thickness 3 μ) containing: Silver iodobromide emulsion containing the sensitized dye S-6 (average grain size 0.6 μ, AgI content 2 mol%) 1.1 g/m² as silver

Coupler F-6	0.4 g/m²
Coupler F-8	0.8 g/m²
High Boiling Point Organic Solvent Oil-1	0.23 cc/m²
Dye D-5	0.02 g/m²

Twelfth Layer (First Protective Layer)

A gelatin layer (dry film thickness 2 μ) containing: Ultraviolet Absorber U-1 0.02 g/m²

Ultraviolet Absorber U-2	0.32 g/m²
Ultraviolet Absorber U-3	0.03 g/m²
High Boiling Point Organic Solvent Oil-2	0.28 cc/m²

Thirteenth Layer (Second Protective Layer)

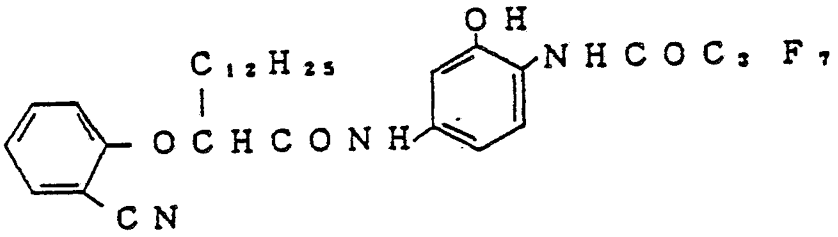
A gelatin layer (dry film thickness 2.5 μ) containing: Fine Grained Silver Iodobromide Emulsion (of which the surface had been fogged; iodide content 1 mol%, average grain size 0.06 μ) 0.1 g/m² as silver

Poly(methyl methacrylate) Grains (average grain size 1.5 μ)

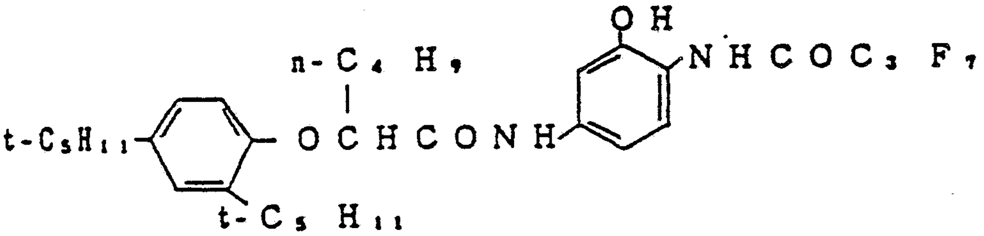
A gelatin hardener H-1 (the same as used in Example 1) and a surfactant were added to each layer as well as the above-mentioned components.

The compounds used to prepare the sample are indicated below.

F-1


OH
NHCOC3F7
C12H25
OCHCONH
CN

F-2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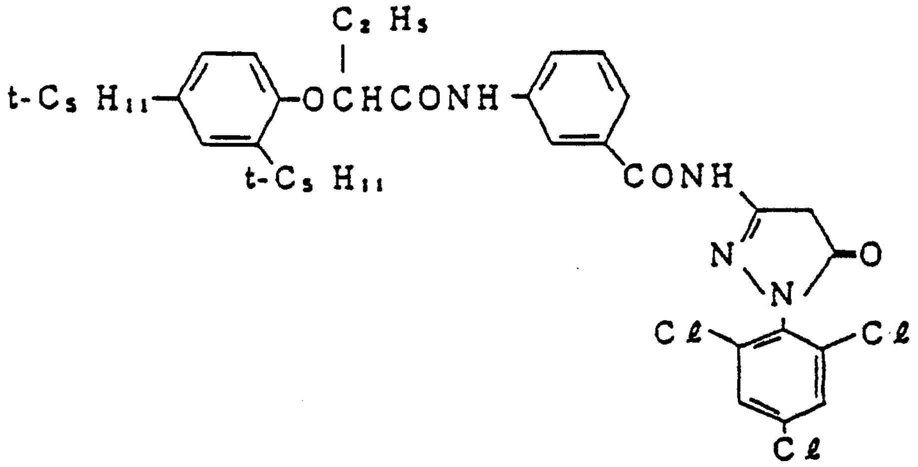
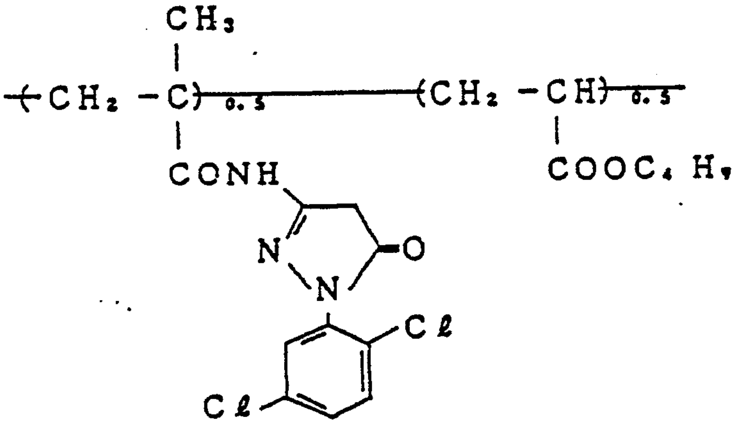
NHCOC3F7
n-C4H9
t-C5H11
OCHCONH
t-C5H11

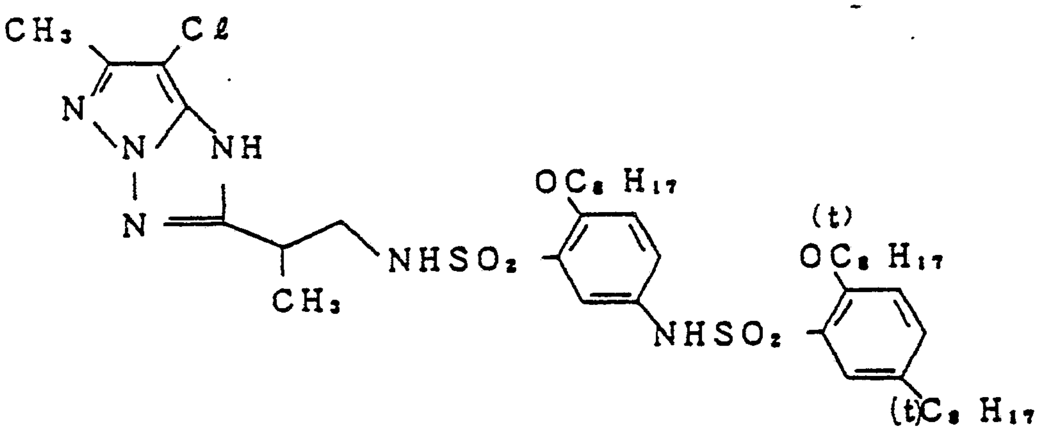
F-3



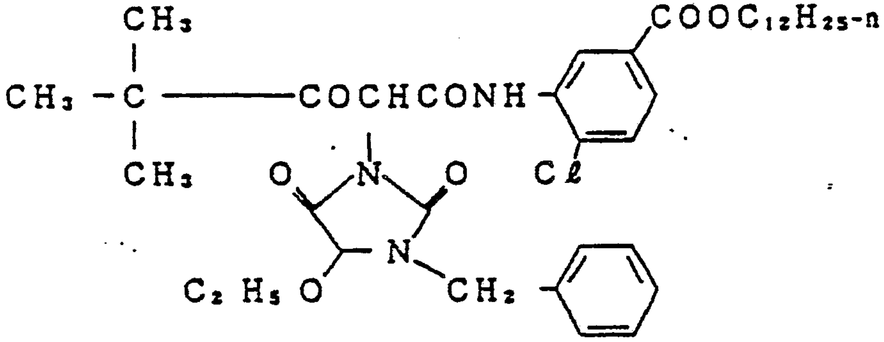
F-4



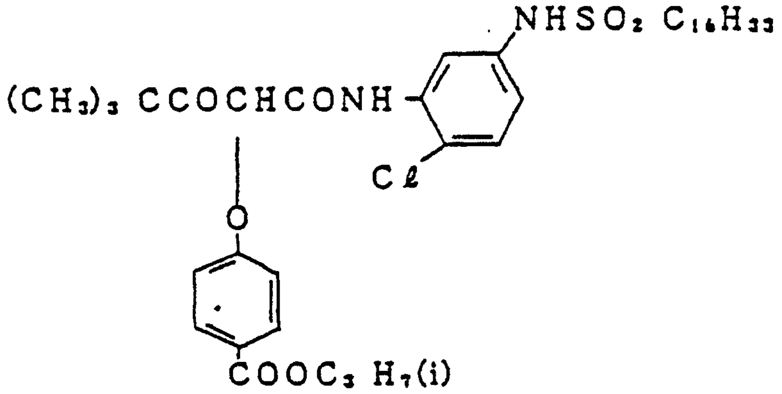
F-5.



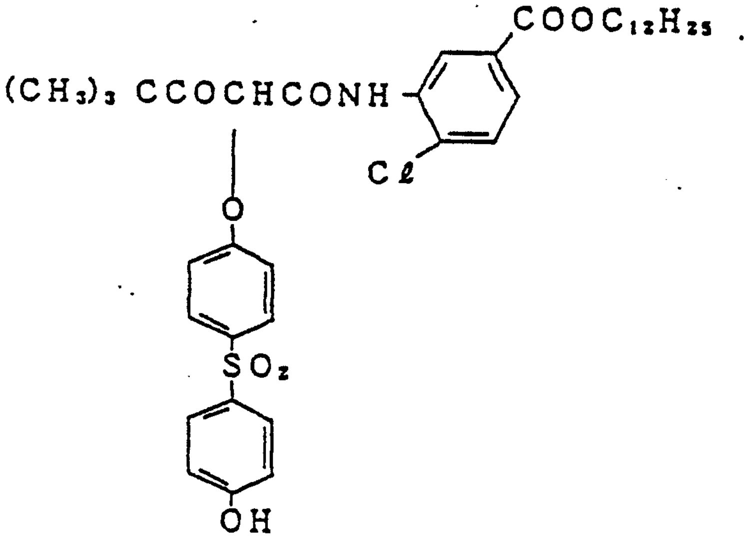
F-6



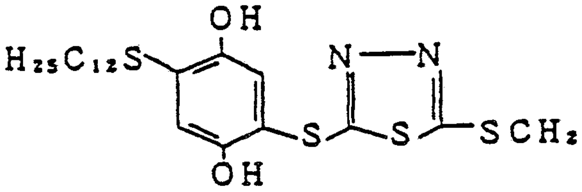
F-7


NHSO₂ C₁₆H₃₃
(CH₃)₃ CCOCHCONH
Cℓ
O
COOC₃ H₇(i)

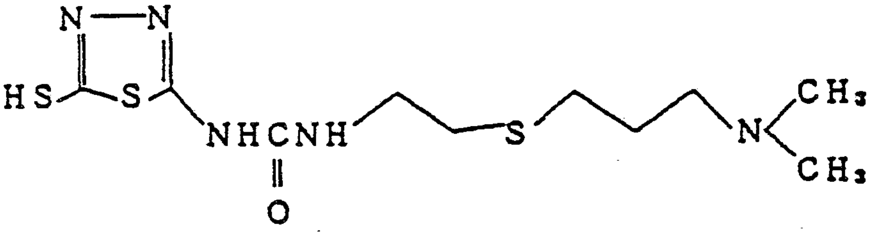
F-8


COOC₁₂H₂₅
(CH₃)₃ CCOCHCONH
Cℓ
O
SO₂
OH

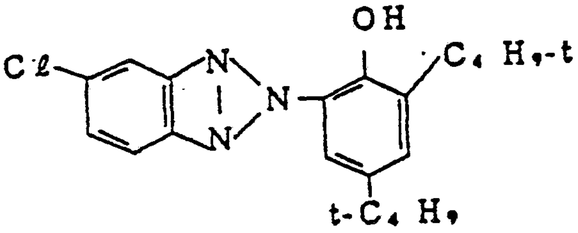
Compound I-1



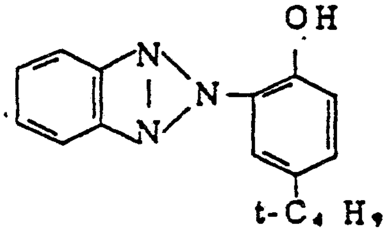
Compound I-2



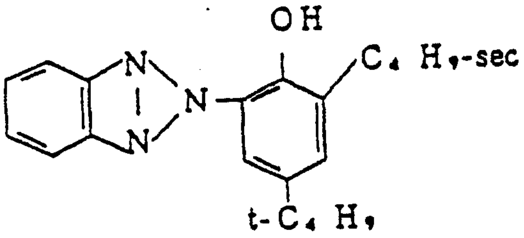
U-1



U-2



U-3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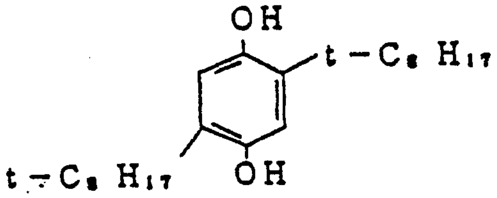
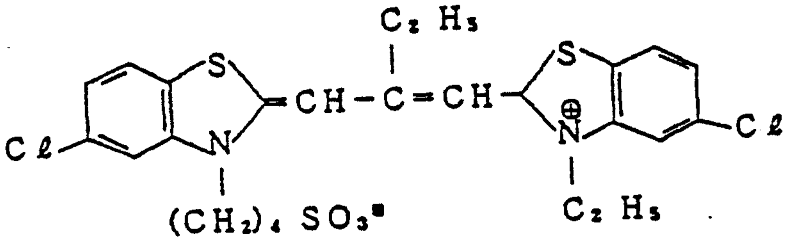
C₄ H₉-sec
N
N
N
t-C₄ H₉

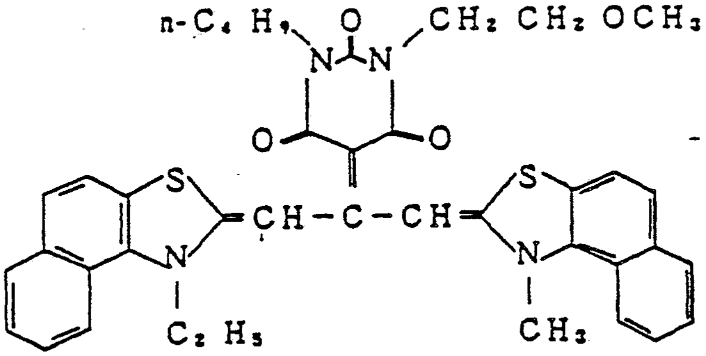
Cpd-C


OH
t-C₈ H₁₇
t-C₈ H₁₇
OH

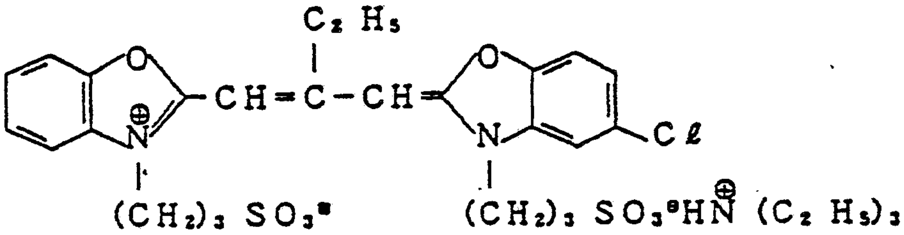
S-1


C₂ H₅
S
CH-C=CH
S
N
Cℓ
(CH₂)₄ SO₃⊖
N⊕
Cℓ
C₂ H₅

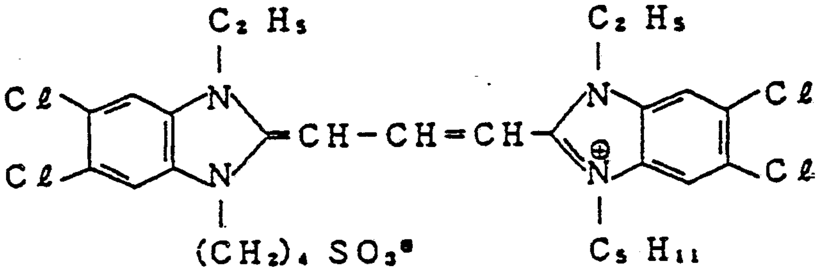
S-2



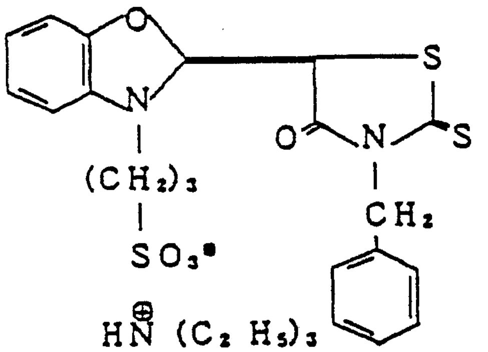
S-3



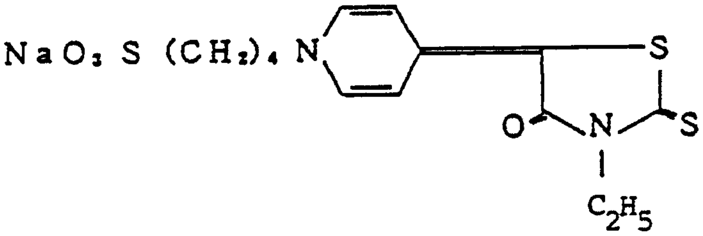
S-4



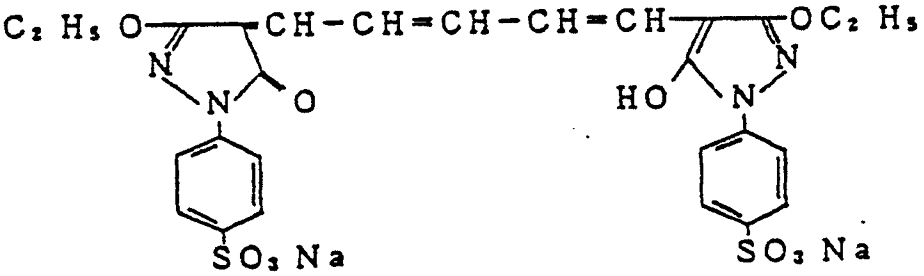
S-5


O
N
S
O
N
S
(CH₂)₃
CH₂
SO₃⊖
HN⊕ (C₂H₅)₃

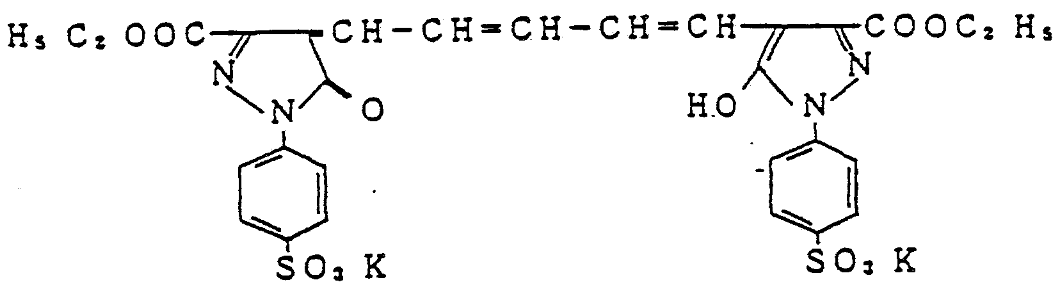
S-6


NaO₃S(CH₂)₄N
S
O
N
S
C₂H₅

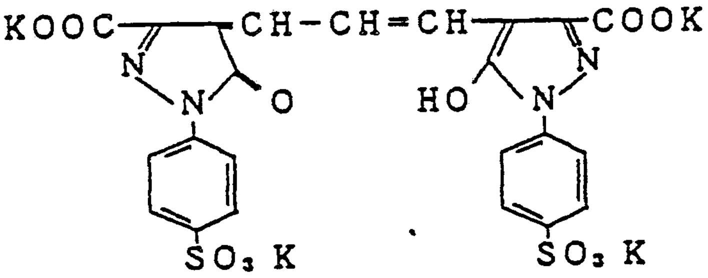
D-1


C₂H₅O
CH-CH=CH-CH=CH
OC₂H₅
N
N
O
HO
N
N
SO₃Na
SO₃Na

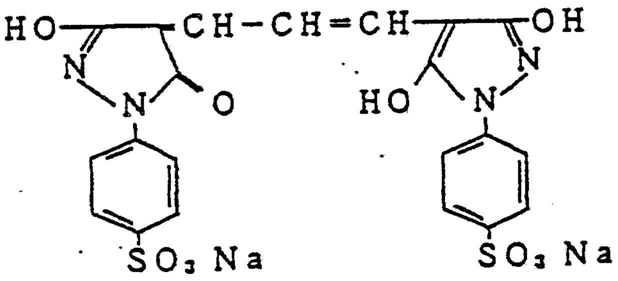
D-2



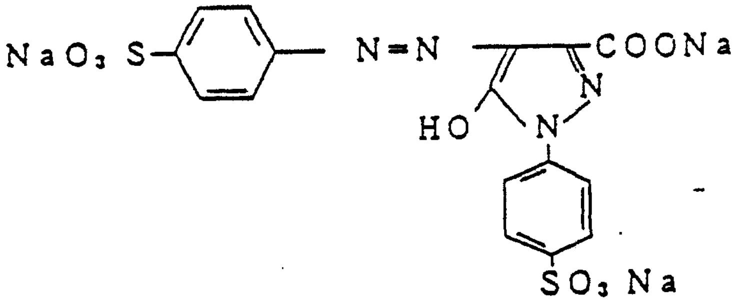
D-3



D-4



D-5



Oil-1 Tricresyl phosphate

Oil-2 Dibutyl phthalate

Preparation of Samples 402 and 403

Sample 402 and 403 were prepared using equimolar amounts of the comparative compounds B-2 and B-3 of Example 1 in place of the Cpd-C in the second, fifth and eighth layer of Sample 401.

Preparation of Samples 404 to 406

Samples 404 to 406 were prepared using equimolar amounts of the compounds A-2, A-3 and A-11, respectively, in place of Cpd-C in the second, fifth and eighth layers of Sample 401.

The Samples 401 to 406 prepared in the way described above were subjected to a red image exposure using a wedge with which the gray density varied continuously and then to a reversal development of the type outlined below.

Processing Operation

Process	Time	Temperature
First Development	6 min.	38°C
Wash	2 min.	38°C
Reversal	2 min.	38°C
Color Development	6 min.	38°C
Conditioning	2 min.	38°C

Bleach	6 min.	38°C
Fix	4 min.	38°C
Wash	4 min.	38°C
Stabilization	1 min.	Ambient
Drying		

The compositions of the processing baths were as follows:

First Development Bath (pH 9.60) Water	700 ml
Nitrilo-N,N,N-trimethylenephosphonic Acid Penta-sodium Salt	2 g
Sodium Sulfite	20 g
Hydroquinone Monosulfonate	30 g
Sodium Carbonate (monohydrate)	30 g
1-Phenyl-4-metnyl-4-hydroxymethyl-3-pyrazolidone	2 g
Potassium Bromide	2.5 g
Potassium Thiocyanate	1.2 g
Potassium Iodide (0.1% solution)	2 ml
Water to make	1000 ml

Reversal Bath(pH 6.00) Water	700 ml
Nitrilo-N,N,N-trimethylenephosphonic Acid Penta-sodium Salt	3 g
Stannous Chloride (dihydrate)	1 g
p-Aminophenol	0.1 g
Sodium Hydroxide	8 g
Glacial Acetic Acid	15 ml
Water to make	1000 ml

Color Development Bath (pH 11.80) Water	700 ml
Nitrilo-N,N,N-trimethylenephosphonic Acid Penta-sodium Salt	3 g
Sodium Sulfite	7 g
Trisodium Phosphate (dodecahydrate)	36 g
Potassium Bromide	1 g
Potassium Iodide (0.1% aqueous solution)	90 ml
Sodium Hydroxide	3 g
Citrazinic Acid	1.5 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate	11 g
3,6-Dithiaoctane-1,8-diol	1 g
Water to make	1000 ml

Conditioning Bath (pH 6.20) Water	700 ml
Sodium Sulfite	12 g
Ethylenediamine Tetraacetic Acid Sodium (dihydrate)	8 g
Thioglycerine	0.4 ml
Glacial Acetic Acid	3 ml
Water to make	1000 ml

Bleach Bath (pH 5.70) Water 800 ml
Ethylenediamine Tetraacetic Acid Sodium (dihydrate) 2 g
Ethylenediamine Tetraacetic Acid Iron(III) Ammonium (dihydrate) 120 g
Potassium Bromide 100 g
Water to make 1000 ml

Fixing Bath (pH 6.60) Water 800 ml
Sodium Thiosulfate 80.0 g
Sodium Sulfite 5.0 g
Sodium Bisulfite 5.0 g
Water to make 1000 ml

Stabilizer BathWater 800 ml
Formaldehyde (37 wt% aq. soln) 5.0 ml
Fuji "Drywell (a surfactant made by the Fuji Film Co., Ltd.; Poly(oxyethylene) p-monononyl phenyl ether; average degree of polymerization ; 10) 5.0 ml
water to make 1000 ml

The maximum color density (Dmax) and the minim color density (Dmin) obtained densitometrically using a red filter were measured for each of the processed samples. Furthermore, the maximum color densities of the blue sensitive layer and the green sensitive layer were each measured using a blue filter and a green filter.

The results obtained are shown in Table 4 below.

Table 4

	Red-Sensitive Layer		Green Sensitive	Blue Layers,
Sample	Dmax	Dmin	Dmax	Dmax
401 (Comparative Ex.)	2.98	0.44	2.64	2.84
402 (")	2.94	0.43	2.60	2.80
403 (")	2.91	0.47	2.61	2.82
404 (This Invention)	2.85	0.35	2.62	2.81
405 (")	2.83	0.38	2.60	2.79
406 (")	2.87	0.40	2.61	2.81

It is clear from Table 4 that Samples 404 to 406 in which compounds of this invention have been used have a lower minimum density (Dmin) for the red-sensitive layer than the Comparative Samples 401 to 403. This indicates that the compounds of this invention are effective for the prevention fo color staining.

EXAMPLE 5

Preparation of Sample 501

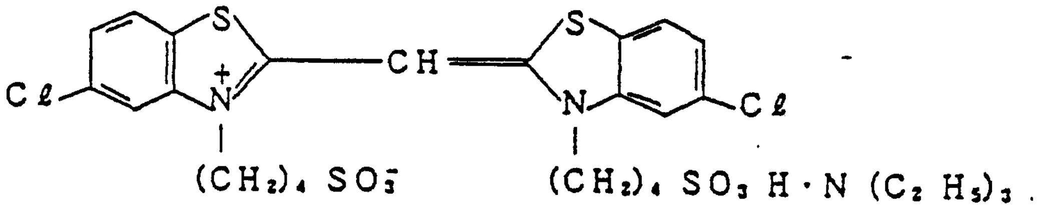
A multi-layer printing paper with the layer structure shown in Table 5 was formed on a paper support which had been laminated on both sides with polyethylene. The coated liquids were prepared in the way indicated below.

Preparation of the First Coating Liquid

Ethyl acetate (27.2 cc) and 7.7 cc of solvent (c) were added to 23.8 mmol of the yellow coupler (a) and 4.4 g of the colored image stabilizer (b) to form a solution which was then emulsified and dispersed in 185 cc of a 10% aqueous gelatin solution which contained 8 cc of 10% sodium dodecylbenzenesulfonate. On the other hand, the blue sensitive sensitizing dye indicated below was added at the rate of 5.0×10^{-4} mol per mol of silver to a silver chlorobromide emulsion (90.0 mol% silver bromide, containing 70 g of silver per kilogram). This emulsion was mixed with the aforementioned emulsified dispersion to form a solution which formed the first layer coating liquid with the composition shown in Table 5. The coating liquids for the second to the seventh layers were prepared using a similar method to that used for the first layer coating liquid. 1-Oxy-3,5-dichloro-s-triazine sodium salt was used as a gelatin hardener for each layer.

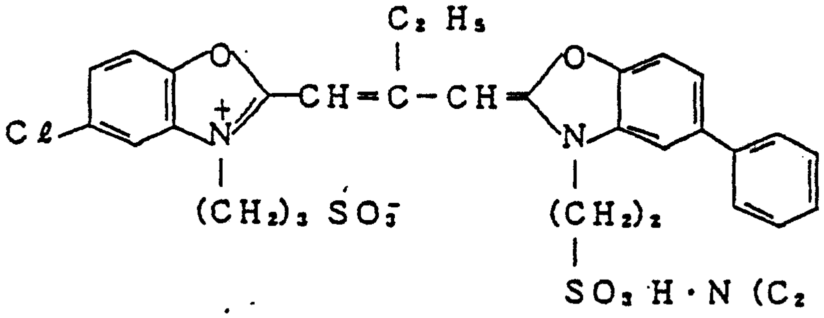
The spectral sensitizing dyes indicated below were used for the various layers.

Blue Sensitive Emulsion Layer



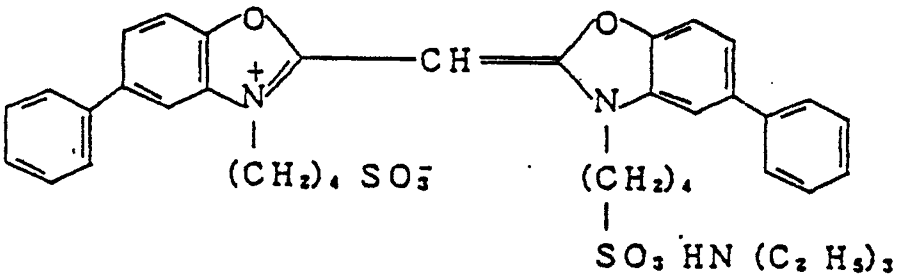
(5.0 x 10^{-4} mol per mol of silver halide)

Green Sensitive Emulsion Layer



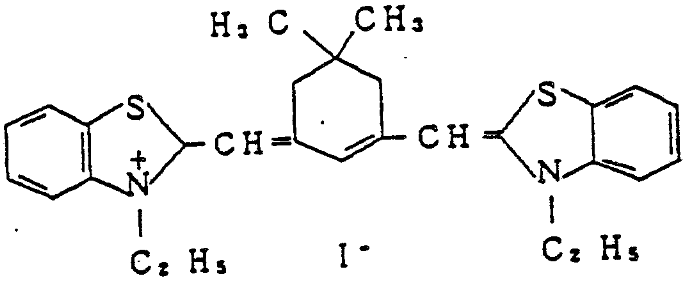
(4.0 x 10^{-4} mol per mol of silver halide)

and



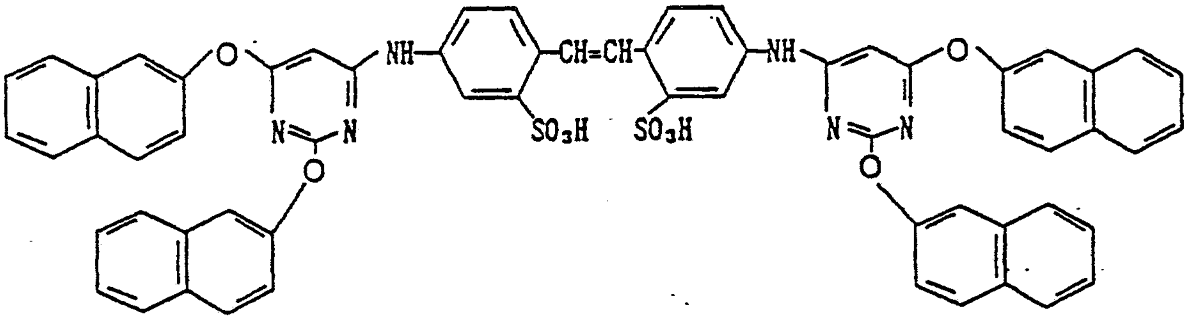
(7.0 x 10^{-5} mol per mol of silver halide)

Red Sensitive Emulsion Layer



(0.9 x 10^{-4} mol per mol of silver halide)

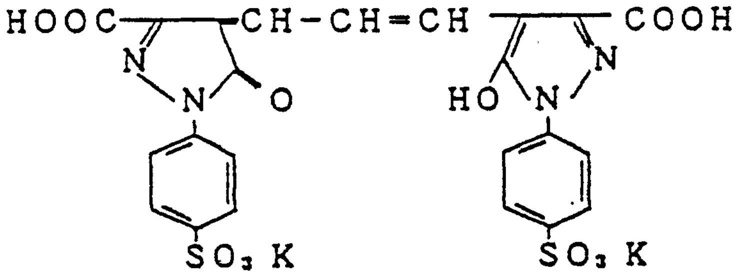
The compound indicated below was added at the rate of 2.6 × 10^{-3} mol per mol of silver halide to the red sensitive emulsion layer.



Furthermore, 1-(5-methylureidophenyl)-5-mercaptotetrazole was added at the rate of 8.5 × 10^{-5} mol, 7.7 × 10^{-4} mol and 2.5 × 10^{-4} mol per mol of silver halide to prepare the blue, green and red sensitive emulsion layers, respectively.

Furthermore, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added at the rate of 1.2 × 10^{-2} mol and 1.1 × 10^{-2} mol per mol of silver halide to the blue and green sensitive emulsion layers, respectively.

The dyes indicated below were added to the emulsion layers prevent the occurrence of irradiation.


HOOC
CH−CH=CH
COOH
N
N
O
HO
N
N
SO₃ K
SO₃ K

and

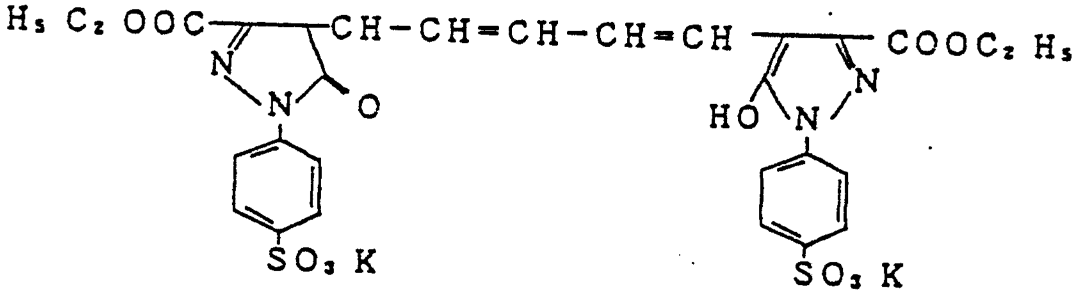
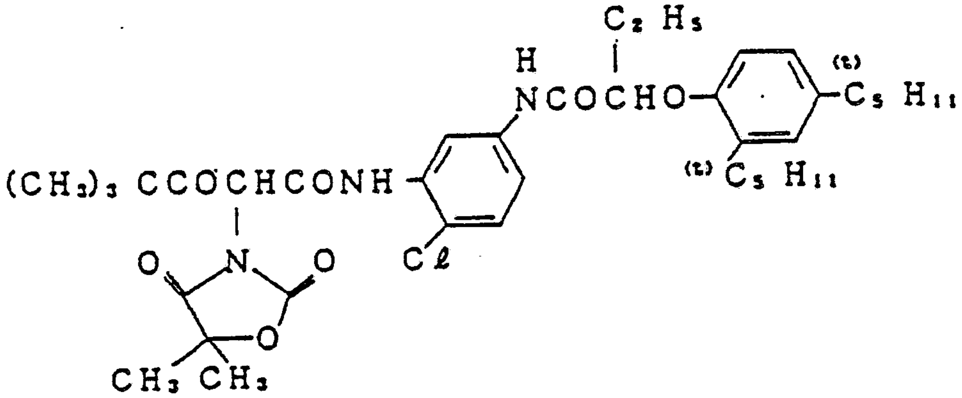

H₅ C₂ OOC
CH−CH=CH−CH=CH
COOC₂ H₅
N
N
O
HO
N
N
SO₃ K
SO₃ K

Table 5

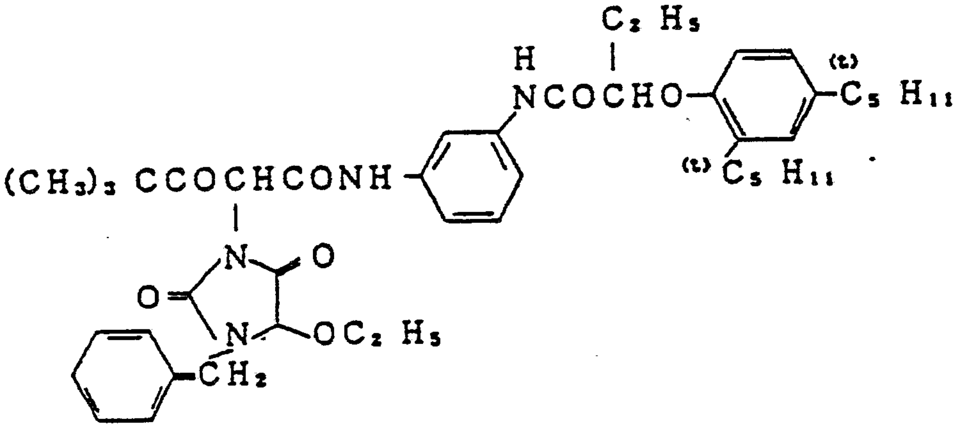
Layer	Principal Composition	Amount Used
Seventh Layer (Protective Layer)	Gelatin	1.33 g/m^2
	Acrylic modified copolymer or poly(vinyl alcohol) (Modification 17%)	0.17 g/m^2
	Liquid paraffin	0.03 g/m^2
Sixth Layer (Ultraviolet Absorbing Layer)	Gelatin	0.53 g/m^2
	Ultraviolet absorber (i)	0.21 g/m^2
	Solvent (k)	0.08 g/m^2
Fifth Layer (Red-sensitive Layer)	Silver halide emulsion	0.23 g/m^2 as silver
	Gelatin	1.34 g/m^2
	Cyan coupler (ℓ)	0.34 g/m^2
	Colored image stabilizer (m)	0.17 g/m^2
	Polymer (n)	0.40 g/m^2
	Solvent (o)	0.23 g/m^2
Fourth Layer (Ultraviolet Absorbing Layer)	Gelatin	1.58 g/m^2
	Ultraviolet absorber (i)	0.62 g/m^2
	Compound (d)	0.05 g/m^2
	Solvent (k)	0.24 g/m^2
Third Layer (Green-Sensitive Layer)	Silver halide emulsion	0.16 g/m^2 as silver
	Gelatin	1.79 g/m^2
	Magenta coupler (e)	0.32 g/m^2
	Colored image stabilizer (f)	0.20 g/m^2
	Colored image stabilizer (g)	0.01 g/m^2

	Solvent (h)	0.65 g/m^2
Second Layer (Anti-Color Mixing Layer)	Gelatin	0.99 g/m^2
	Compound (d)	0.08 g/m^2
First Layer (Blue-Sensitive Layer)	Silver halide emulsion	0.26 g/m^2 as silver
	Gelatin	1.83 g/m^2
	Yellow coupler (a)	0.50 mmol/m^2
	Yellow coupler (j)	0.50 mmol/m^2
	Colored image stabilizer (b)	0.11 g/m^2
	Solvent (c)	0.35 g/m^2
Support	Polyethylene laminated paper White pigment (TiO_2) and blue dye (Ultramarine) included in the polyethylene on the side of the first layer	

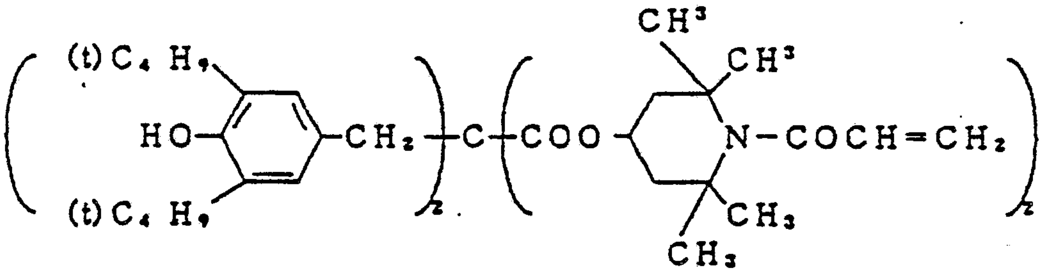
(a) Yellow Coupler



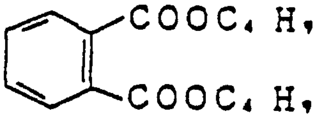
(j) Yellow Coupler



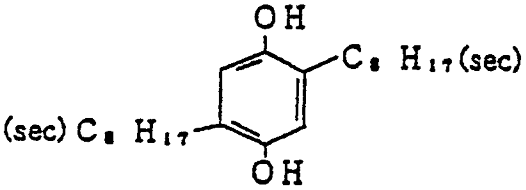
(b) Colored Image Stabilizer



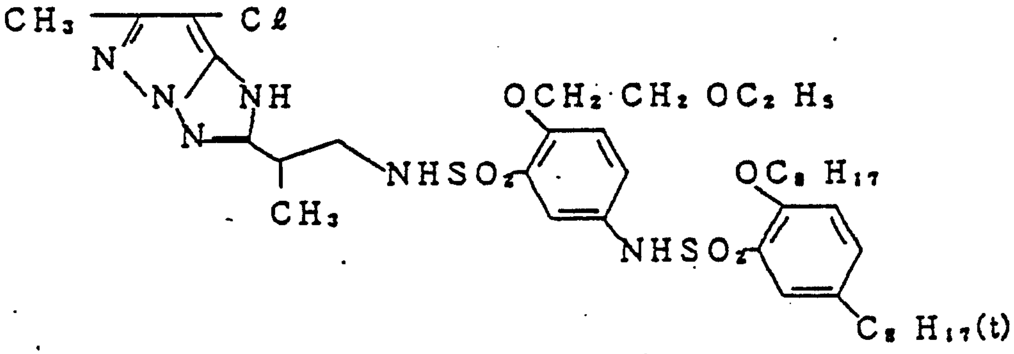
(c) Solvent



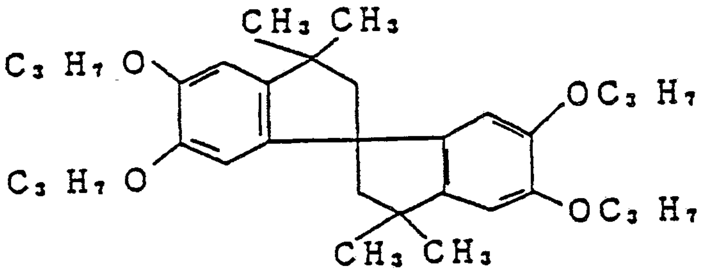
(d)



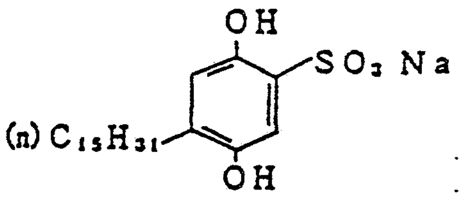
(e) Magenta Coupler



(f) Colored Image Stabilizer

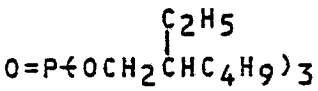


(g) Colored Image Stabilizer



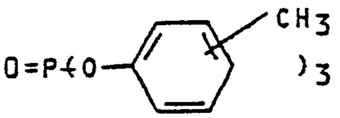
(h) Solvent

A 2 : 1 (by volume) mixture of



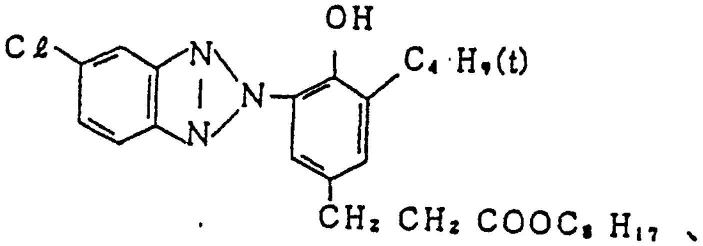
$O{=}P{\leftarrow}OCH_2\underset{}{\overset{C_2H_5}{|}}{CH}C_4H_9)_3$

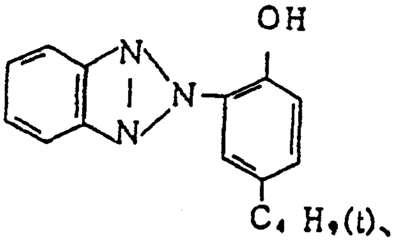
and



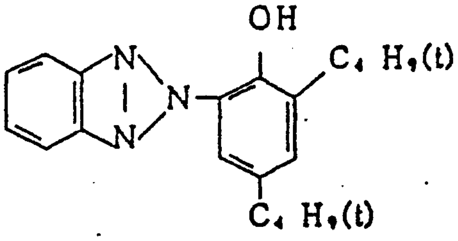
(i) Ultraviolet Absorber

A2 : 9 : 8 (by weight) mixture of





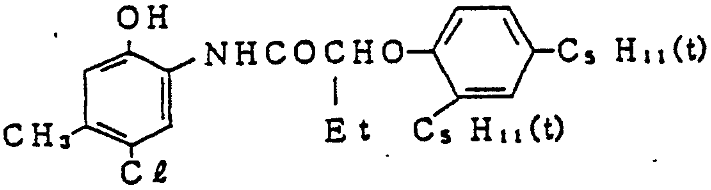
and



(k) Solvent

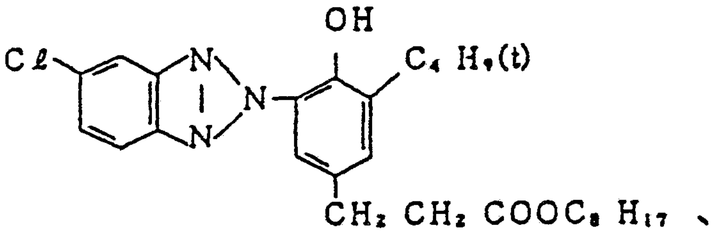
$O=P-(O-C_9H_{19}(iso))_3$

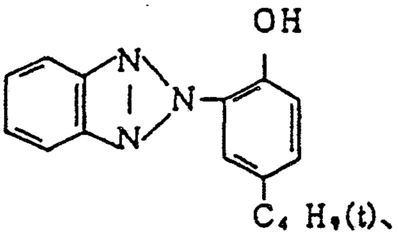
(ℓ) Cyan Coupler



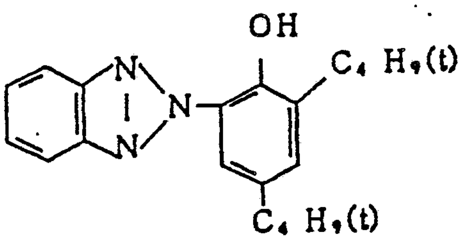
(m) Colored Image Stabilizer

A5 : 8 : 9 (by weight) mixture of





and

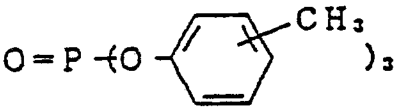


(n) Polymer

$\left(CH_2-\underset{\displaystyle CONHC_4H_9(t)}{CH} \right)_n$

Average molecular weight 35,000

(o) Solvent



Preparation of Samples 502 and 503

Samples 502 and 503 were prepared using an equimolar amount of the comparative compound B-2 of Example 1 and the compound Cpd-A of Sample 101 in place of the compound (d) in the second and fourth layers of Sample 501.

Preparation of Samples 504 to 506

Samples 504 to 506 were prepared using the compounds A-3, A-10 and A-14 of this invention in place of the compound (d) in the second and fourth layers of Sample 501.

Afte an image exposure, the above mentioned photosensitive materials were processed continuously (in a running test) using a paper processor in accordance with the processing treatment indicated below until the amount of replenisher used was twice the color development tank capacity. Subsequently the above mentioned photosensitive materials were given a red image exposure and developed using the same processing baths.

Processing Step	Time (sec.)	Temp. (°C)	Tank Volume (ℓ)	Replenisher Amount (ml)
Color Development	45	35	17	161
Bleach-Fix	45	30-36	17	161
Rinse (1)	20	30-37	10	-
Rinse (2)	20	30-37	10	-
Rinse (3)	20	30-37	10	-
Rinse (4)	30	30-37	10	248
Drying	60	70-80		

Per square meter of photosensitive material

(Three tank counter-flow system rinse (4)→(1))

The compositions of the processing baths were as follows:

Color Development Bath

	Tank Solution	Replenisher Solution
Water	800 ml	800 ml
Ethylenediamine-N,N,N',N'-tetramethylenephosphonic Acid	1.5 g	1.5 g
DABCO	6.0 g	6.0 g
Potassium Bromide	1.4 g	
Potassium Carbonate	25 g	25 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate	5.0 g	7.0 g
Diethylhydroxylamine	4.2 g	6.0 g

Fluorescent Whitener (4,4-diaminostilbene based)	2.0 g	2.5 g
Water to make	1000 ml	1000 ml
pH (25°C)	10.05	10.45

Bleach Fix Bath (Tank and Replenisher Solutions were the same)

Water	400 ml
Ammonium Thiosulfate (70%)	100 ml
Sodium Sulfite	17 g
Ethylenediamine Tetraacetic Acid Iron (III) ammonium Salt	55 g
Ethylenediamine Tetraacetic Acid Di-sodium Salt	5 g
Ammonium Bromide	40 g
Glacial Acetic Acid	9 g
Water to make	1000 ml
pH (25°C)	5.40

Rinse bath (Tank and Replenisher Solutions were the same)Ion exchange water (Calcium and magnesium contents both below 3 ppm).

Each of the developed samples was subjected to density measurements using a green filter. The difference (D_1-D_2) between the magenta density (D_1) at the maximum cyan color density and the magenta density (D_2) at the minimum cyan color density was measured and the results are shown in Table 6.

Table 6

Sample	Difference (D_1 - D_2)	
501	0.20	For Comparison
502	0.21	"
503	0.18	"
504	0.15	This Invention
505	0.13	"
506	0.17	"

A smaller value for the difference (D_1-D_2) indicates a lower color turbidity. It is clear from Table 6 that the Samples 504 to 506 in which compounds of this invention had been used had lower levels of color turbidity than the Comparative Samples 501 to 503.

This result indicates that the compounds of this invention are effective for reducing color turbidity.

EXAMPLE 6

After exposing Sample 401 prepared in Example 4 described above, the sample was processed by the process described below using an automatic processor until the total replenisher amount for the 1st developer became thrice the volume of the tank. Thereafter, each of Samples 401 to 406 prepared in Example 4 was imagewise red exposured using a wedge continuously changing grey density and then processed by the process described below.

Processing Step	Time	Temp.	Tank Volume (ℓ)	Replenisher Amount
1st Development	6 min.	38°C	12	2200 ml/m^2
1st Wash	45 sec.	38°C	2	2200 ml/m^2
Reversal	45 sec.	38°C	2	1100 ml/m^2
Color Development	6 min.	38°C	12	2200 ml/m^2
Bleach	2 min.	38°C	4	860 ml/m^2
Blix	4 min.	38°C	8	1100 ml/m^2
2nd Wash (1)	1 min.	38°C	2	-
2nd Wash (2)	1 min.	38°C	2	1100 ml/m^2
Stabilization	1 min.	25°C	2	1100 ml/m^2
Drying	1 min.	65°C	-	-

In this case, the replenishing system was carried out by a so-called countercurrent replenishing system wherein the replenisher for the 2nd wash was introduced into 2nd wash (2) and the overflow liquid from 2nd wash (2) was introduced into 2nd wash (1).

The composition of each processing solution used in the aforesaid processing step was as follows.

1st Developer

	Mother Liquor	Replenisher
Nitrilo-N,N,N-trimethylenephosphonic Acid Penta-sodium Salt	2.0 g	2.0 g
Sodium Sulfite	30 g	30 g

Hydroquinone.Potassium Monosulfonate	20 g	20 g
Potassium Carbonate	33 g	33 g
1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	2.0 g	2.0 g
Potassium Bromide	2.5 g	1.4 g
Potassium Thiocyanate	1.2 g	1.2 g
Potassium iodide	2.0 mg	-
Water to make	1000 ml	1000 ml
pH	9.60	9.60

The pH was adjusted with hydrochloric acid or potassium hydroxide.

1st Wash Water

	Mother Liquor	Replenisher
		Same as the mother liquor
Ethylenediaminetetramethylenephosphonic Acid	2.0 g	
Di-sodium Phosphate	5.0 g	
Water to make	1000 ml	
pH	7.00	

The pH was adjusted with either hydrochloric acid or sodium hydroxide.

Reversal Solution

	Mother Liquor	Replenisher
		Same as the mother liquor
Nitrilo-N,N,N-trimethylenephos-		

phonic Acid.Penta-sodium Salt	3.0 g
Stannous Chloride.Di-hydrate	1.0 g
p-Aminophenol	0.1 g
Sodium Hydroxide	8 g
Glacial Acetic Acid	15 ml
Water to make	1000 ml
pH	6.00

The pH was adjusted with hydrochloric acid or sodium hydroxide.

Color Developer

	Mother Liquor	Replenisher
Nitrilo-N,N,N-trimethylenephosphonic Acid,Penta-sodium Salt	2.0 g	2.0 g
Sodium Sulfite	7.0 g	7.0 g
Tri-Sodium Phosphate.$12H_2O$	36 g	36 g
Potassium Bromide	1.0 g	-
Potassium Iodide	90 mg	-
Sodium Hydroxide	3.0 g	3.0 g
Citrazinic Acid	1.5 g	1.5 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate	11 g	11 g
3,6-Dithiaoctane-1,8-diol	1.0 g	1.0 g
Water to make	1000 ml	1000 ml
pH	11.80	12.00

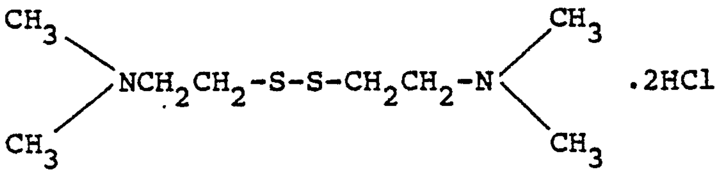
The pH was adjusted with hydrochloric acid or potassium hydroxide.

Bleach Solution

	Mother Liquor	Replenisher
		Same as the mother liquor
Ethylenediaminetetraacetic Acid.Di-sodium Salt.Di-hydrate	10.0 g	
Ethylenediaminetetraacetic Acid.Fe(III).Ammonium.$2H_2O$	120 g	
Ammonium Bromide	100 g	
Ammonium Nitrate	10 g	
Bleach Accelerator*	0.005 mol	
Water to make	1000 ml	
pH	6.30	

The pH was adjusted with hydrochloric acid or aqueous ammonia.

(*): Bleach accelerator:



Blix Solution

	Mother Liquor	Replenisher
		Same as the mother liquor
Ethylenediaminetetraacetic Acid.Fe(III).Ammonium. Di-hydrate	50 g	

Ethylenediaminetetraacetic Acid.Di-sodium.Di-hydrate	5.0 g
Sodium Thiosulfate	80 g (Same as the mather liquor)
Sodium Sulfite	12.0 g
Water to make	1000 ml
pH	6.60

The pH was adjusted with hydrochloric acid or aqueous ammonia.

2nd Wash Water: The mother liquor was same as replenisher

City water was passed through a mixed bed system column packed with a H-type strong cation exchange resin (Amberlite IR-120B), trade name, made by Rhom and Haas Co.) and an OH-type anion exchange resin (Amberlite IR-400 made by Rhom and Haas Co.) to reduce the concentrations of calcium and magnesium less than 3 ml/liter and then 20 mg/liter of sodium dichloroisocyanurate and 1.5 g/liter of sodium sulfate were added thereto. The pH of the solution was in the range of from 6.5 to 7.5.

Fix Solution

	Mother Liquor	Replenisher
		Same as the mother liquor
Formalin (37%)	5.0 ml	
Polyoxyethylene-p-monononyl-phenyl ether (mean molecular weight 10)	0.5 ml	
Water to make	1000 ml	
pH	not adjusted.	

On each of the samples thus processed, the maximum color density (Dmax) and the minimum density (Dmin) were measured using a red filter. Also, the maximum color densities of the blue-sensitive layer and the green-sensitive layer of each sample were measured using a blue filter and green filter, respectively. The results were almost same as those shown in Table 4 above.

EXAMPLE 7

A multilayer silver halide photographic material (Sample 601) having the following layers on a paper support having polyethylene coating on both surfaces thereof was prepared. The coating compositions for the layers were prepared as follows.

Coating Composition for Layer 1

In a mixture of 27.2 ml of ethyl acetate and 7.7 ml (8.0 g) of high-boiling solvent (Solv-1) were dissolved 10.2 g of yellow coupler (ExY-1), 9.1 g of yellow coupler (ExY-2), and 4.4 g of color image stabilizer (Cpd-1) and the solution was dispersed by emulsification in 185 ml of an aqueous 10% gelatin solution containing 8 ml of an aqueous 10% sodium dodecylbenzenesulfonate. The emulsified dispersion was mixed with Emulsions EM 1 and Em 2 and the gelatin concentration was adjusted to provide the following composition. Thus, a coating composition for layer 1 was prepared.

The coating compositions for layer 2 to layer 7 were also prepared by similar manners as above.

For each layer was used 1-oxy-3,5-dichloro-s-triazine sodium salt as a gelatin hardening agent. As a tackifier (Cpd-2) was used.

Layer Structure

The composition of each layer is shown below. The numerals are coated amount (g/m^2), wherein the silver halide emulsion is shown by the calculated silver amount.

Support:

Polyethylene laminated paper

(The polyethylene coating at the emulsion layer carrying side contained white pigment (TiO_2) and a bluish dye.)

Layer 1 (Blue-Sensitive Layer) Monodispersed Silver Chlorobromide Emulsion (EM 1) spectrally sensitized by sensitizing dye (ExS-1) 0.13
Monodispersed Silver Chlorobromide Emulsion (EM 2) spectrally sensitized by sensitizing dye (ExS-1) 0.13
Gelatin 1.86
Yellow Coupler (ExY-1) 0.44
Yellow Coupler (ExY-2) 0.39
Color Image Stabilizer (Cpd-1) 0.19
Solvent (Solv-1) 0.35

Layer 2 (Color Mixing Prevention Layer) Gelatin 0.99
Color Mixing Preventing Agent (Cpd-3) 0.08

Layer 3 (Green-Sensitive Layer) Monodispersed Silver Chlorobromide Emulsion (EM 4) spectrally sensitized by sensitizing dye (ExS-2, 3) 0.11
Gelatin 1.80
Magenta Coupler (ExM-1) 0.39
Color Image Stabilizer (Cpd-4) 0.20
Solvent (Solv-2) 0.12
Solvent (Solv-3) 0.25

Layer 4 (Ultraviolet Absorptive layer) Gelatin 1.60
Ultraviolet Absorbents (Cpd-7/Cpd-8/Cpd-9 = 3/2/6 by weight ratio) 0.70
Color Mixing Preventing Agent (Cpd-10) 0.05
Solvent (Solv-4) 0.27

Layer 5 (Red-Sensitive Layer) Monodispersed Silver Chlorobromide emulsion (EM6) spectrally sensitized by sensitizing dye (ExS-4, 5) 0.07
Monodispersed Silver Chlorobromide Emulsion spectrally sensitized by sensitizing dye (ExS-4, 5) 0.16
Gelatin 0.92
Cyan Coupler (ExC-1) 0.32
Color Image Stabilizers (Cpd-8/Cpd-9/Cpd-12 = 3/4/2 by weight ratio) 0.17
Dispersing Polymer (Cpd-11) 0.28
Solvent (Solv-2) 0.20

Layer 6 (Ultraviolet Absorptive Layer) Gelatin 0.54
Ultraviolet Absorbents (Cpd-7/Cpd-9/Cpd-12 = 1/5/3 by weight ratio) 0.21
Solvent (Solv-2) 0.08

Layer 7(Protective Layer) Gelatin 1.33
Acryl-modified copolymer of polyvinyl alcohol (modified degree 17%) 0.17
Fluid paraffin 0.03

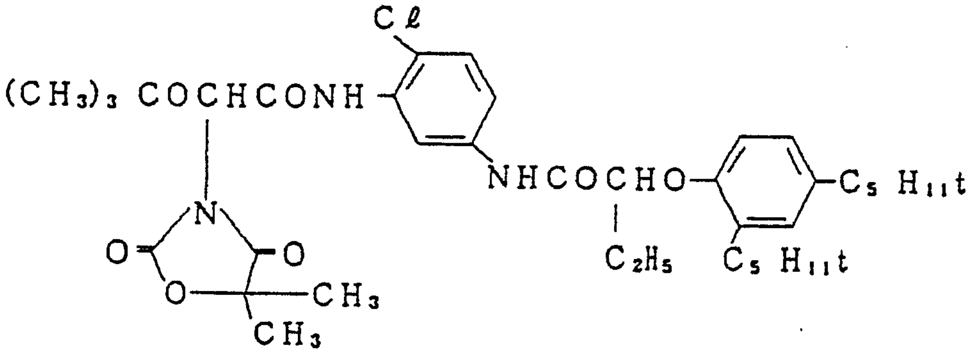
Also, in this case, Cpd-13 and Cpd-14 were used as irradiation preventing dyes. Furthermore, each layer contained Alkanol XC (made by DuPont), sodium alkylbenzenesulfonate, succinic acid ester, and Magefacx F-120 (made by Dainippon Ink and Chemicals, Inc.) as dispersing agent and coating aid. Also, Cpd-15 and Cpd-16 were used as the stabilizers for silver halide.

The emulsions used are as follows.

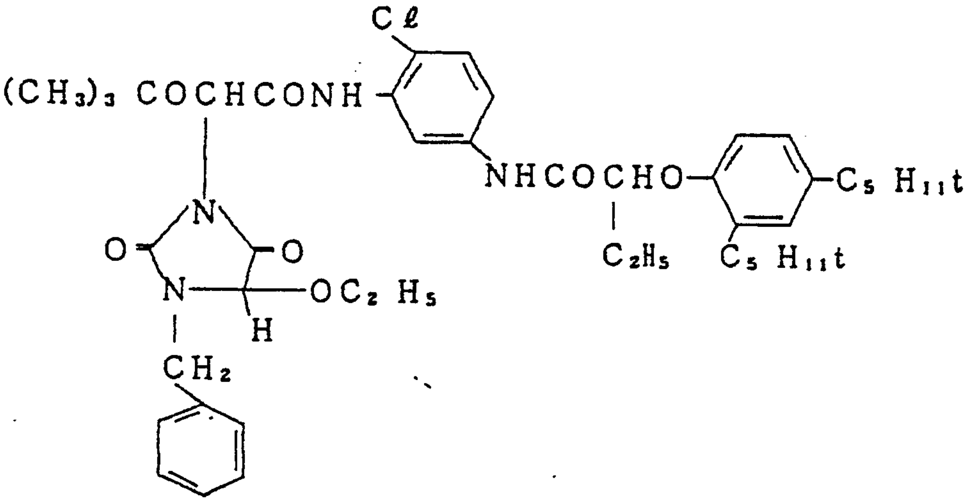
Emulsion	Form	Grain Size	Br Content (mol%)	Variation Coefficient
EM 1	Cube	1.0	80	0.08
EM 2	Cube	0.75	80	0.07
EM 3	Cube	0.5	83	0.09
EM 4	Cube	0.4	83	0.10
EM 5	Cube	0.5	73	0.09
EM 6	Cube	0.4	73	0.10

The compounds used above are as follows.

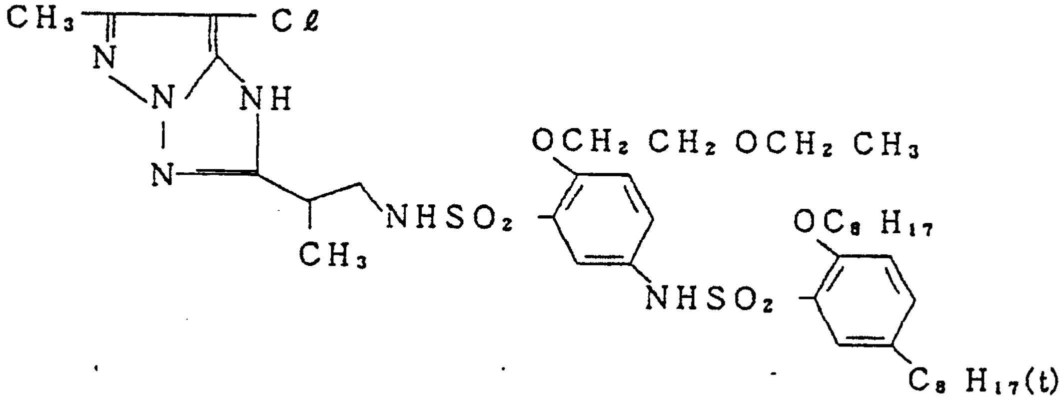
ExY-1



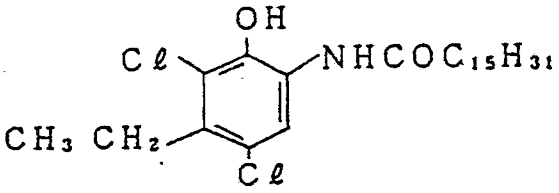
ExY-2



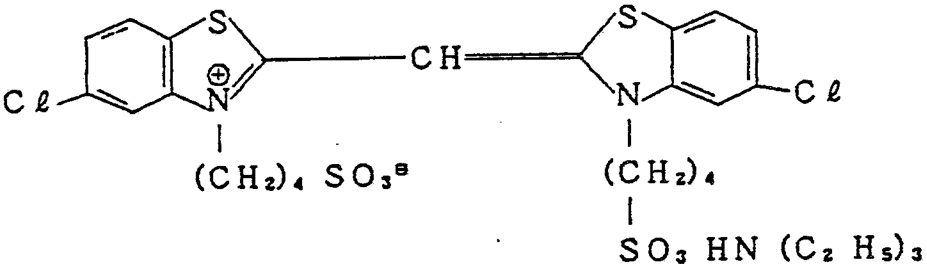
ExM-1



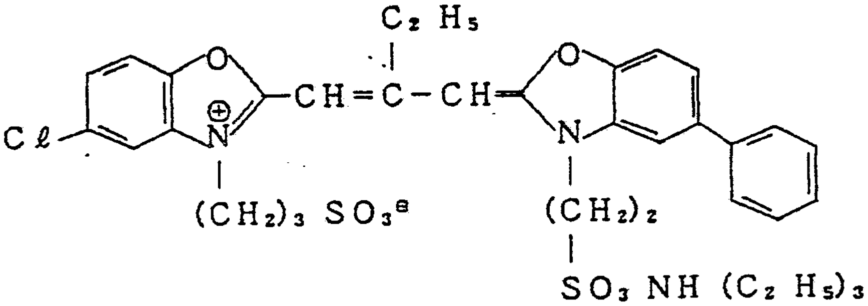
ExC-1



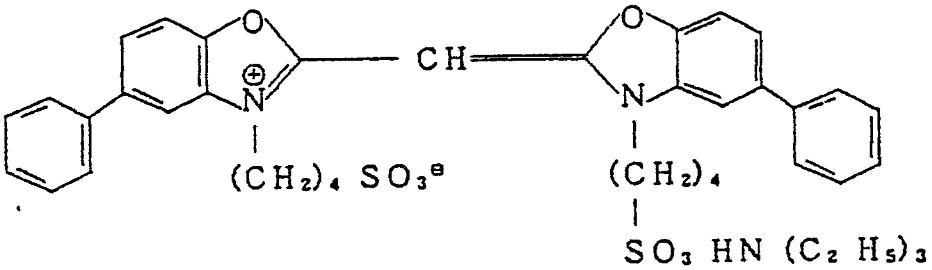
ExS-1



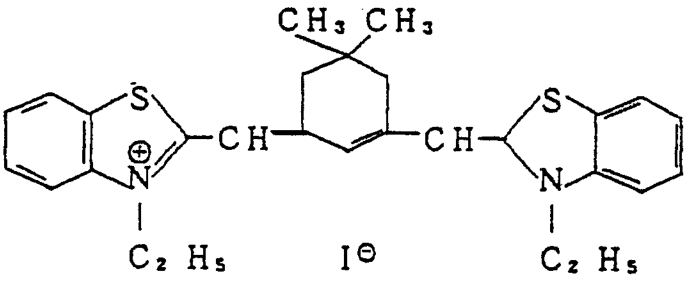
ExS-2



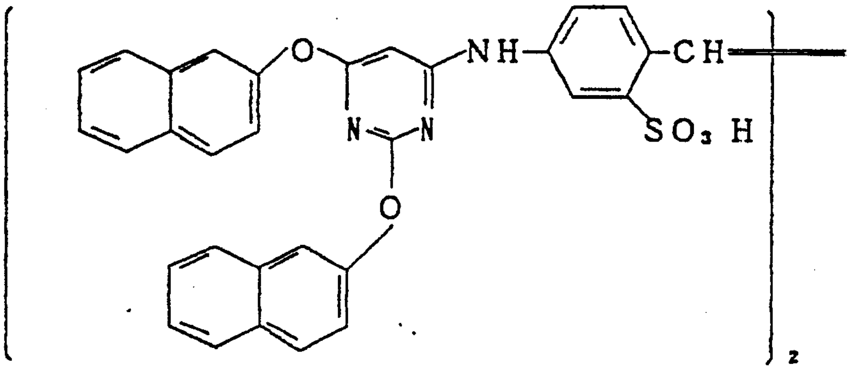
ExS-3



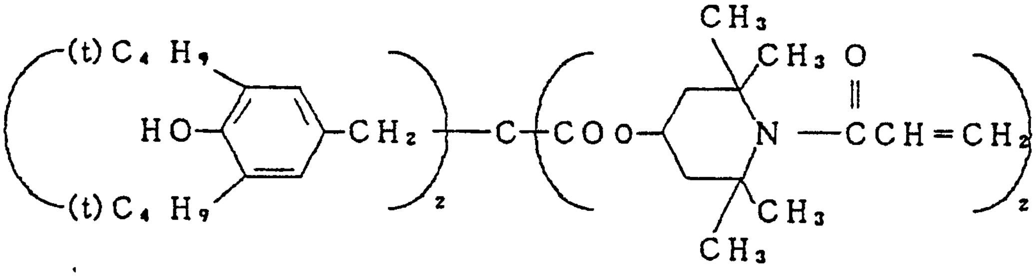
ExS-4



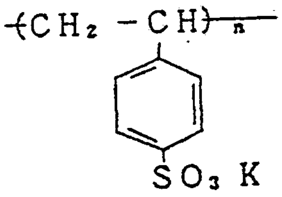
ExS-5



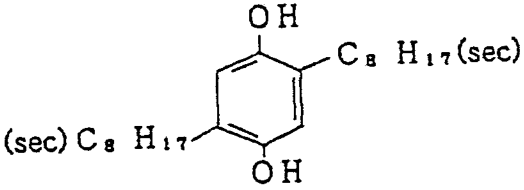
Cpd-1



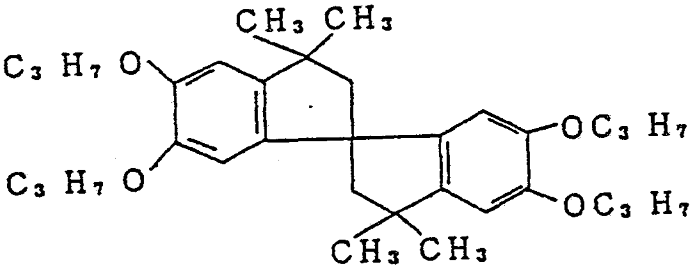
Cpd-2



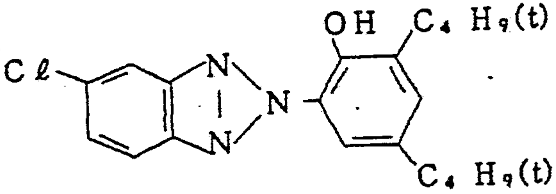
Cpd-3



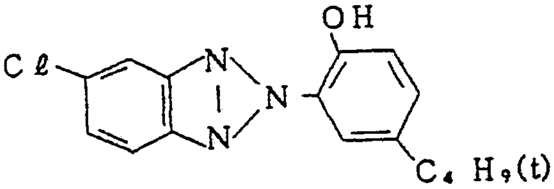
Cpd-4



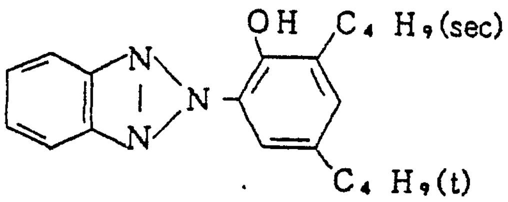
Cpd-7



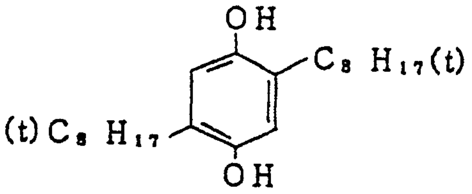
Cpd-8



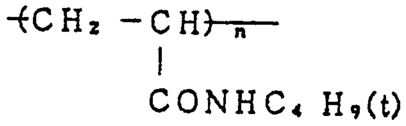
Cpd-9



Cpd-10



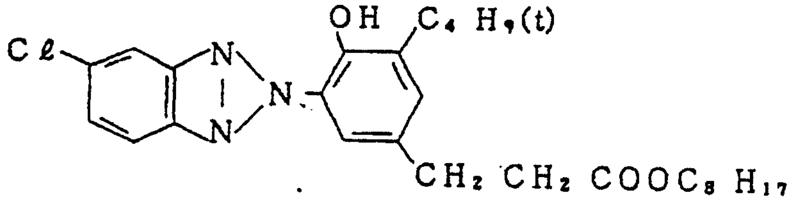
Cpd-11



$$\left(CH_2-\underset{\displaystyle CONHC_4H_9(t)}{\underset{|}{CH}}\right)_n$$

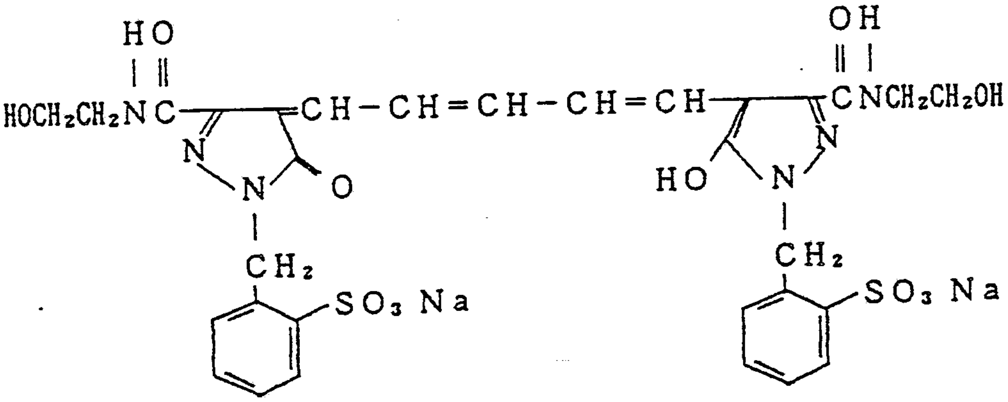
(n = 100 ~ 1000)

Cpd-12

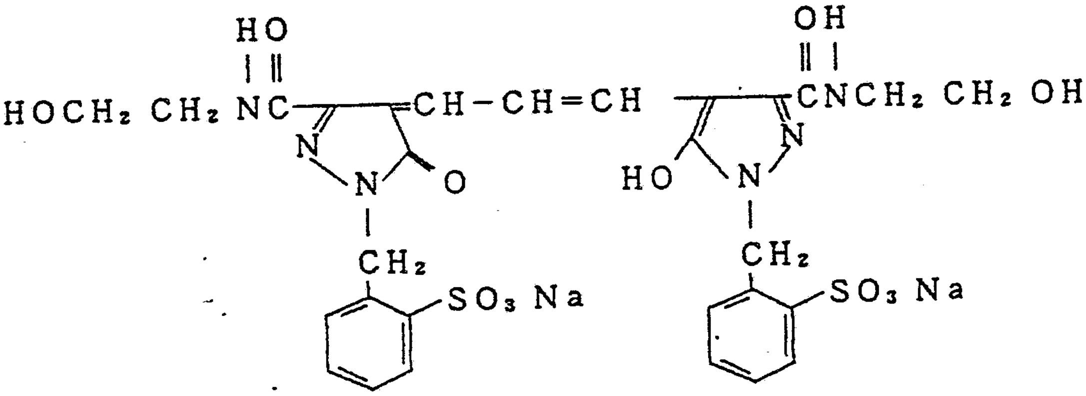


Solv-1	Dibutylphthalate
Solv-2	Tricresylphosphate
Solv-3	Trioctylphosphate
Solv-4	Trinonylphosphate

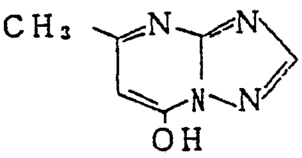
Cpd-13



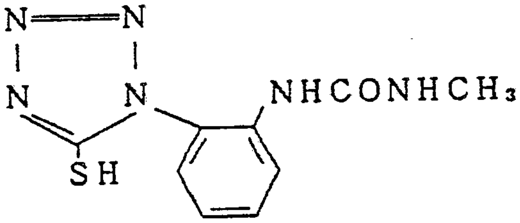
Cpd-14



Cpd-15



Cpd-16



Preparation of Samples 602 and 603

By following the same procedure as Sample 601 while using Comparison Compound B-2 or Compound Cpd-A of Sample 101 in Example 1 in place of Compound Cpd-3 and Cpd-10 in Layer 2 and Layer 4 of Sample 602 in equimolar amount, Samples 602 and 603 were prepared.

Preparation of Samples 604 to 606

By following the same procedure as Sample 601 while using Compound A-3, A-10, or A-14 in place of Cpd-3 and Cpd-10 in Layer 2 and Layer 4 of Sample 601, Samples 604 to 606 were prepared.

Each of the samples was exposed through an optical wedge and a red filter and processed in the following steps.

Processing Step	Temperature	Time
Color Development	38°C	1 min. 40 sec.
Blix	30 ~ 34°C	40 sec.
Rinse 1	30 ~ 34°C	20 sec.
Rinse 2	30 ~ 34°C	20 sec.
Rinse 3	30 ~ 34°C	20 sec.
Drying	70 ~ 80°C	50 sec.

(Countercurrent system for the rinse 3 to 1 using three tanks)

The composition of the processing solutions were as follows.

Color Developer

Water	800 ml
Diethylenetriaminepentaacetic Acid	1.0 g
1-Hydroxyethylidene-1,1-disulfonic Acid (60%)	2.0 g
Nitrilotriacetic Acid	2.0 g
Triethylenediamine(1,4-diazabicyclo(2,2,2)octane)	5.0 g
Potassium Bromide	0.5 g
Potassium Carbonate	30 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate	5.5 g
Diethylhydroxylamine	4.0 g
Optical Whitening Agent (UVTEX-CK, trade name, made by Ciba-Geigy)	1.5 g
Water to make	1000 ml
pH (25°C)	10.25

Blix Solution

Water	400 ml
Ammonium Thiosulfate (70%)	200 ml
Sodium Sulfite	20 g
Ethylenediaminetetraacetic Acid Fe(III).Ammonium	60 g
Ethylenediaminetetraacetic Acid.Di-Sodium	10 g
Water to make	1000 ml
pH (25°C)	10.25

Rinse Solution Ion-exchange water (calcium and magnesium contents were below 3 ppm)

On each sample thus processed, the density was measured using a green filter. The difference (A1-D2) between magenta density (Di) in the cyan maximum color density and magenta density (D2) in the cyan minimum color density was determined and the results is shown in Table 5.

Table 5

Sample	Difference (D1 - D2)	
601	0.22	Comparison
602	0.22	"
603	0.19	"
604	0.16	Invention
605	0.14	"
606	0.17	"

Less value of the difference (D1-D2) shows less color turbidity.

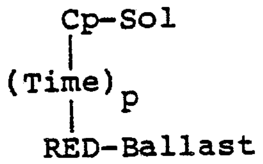
From the results shown in Table 5, it can be seen that Samples 604 to 606 using the compounds of this invention show less color turbidity as compared to Comparison Samples 601 to 603.

The results show that the compounds of this invention are effective for the reduction of color turbidity.

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

Claims

1. A color photographic material comprising a support having provided thereon at least one blue, at least one green and at least one red light-sensitive silver halide emulsion layer and containing in one of said light-sensitive layers or a layer other than said light-sensitive layers a compound represented by formula (A)



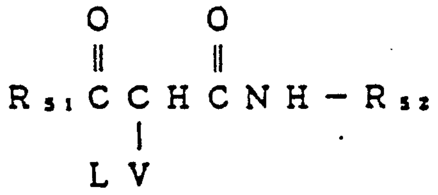
$$\begin{array}{c} \text{Cp-Sol} \\ | \\ (\text{Time})_p \\ | \\ \text{RED-Ballast} \end{array} \qquad (A)$$

wherein, Cp represents a group capable of releasing the $(\text{Time})_p$-RED-Ballast group in a coupling reaction with the oxidized form of the developing agent; RED-ballast is a group capable of being released from Cp group directly or via (Time)p group and reducing the oxidized form of the developing agent; (Time)p represents a timing group; p is either zero or a positive integer; Sol is a group to diffuse a coupling product from a photographic layer; and Ballast is a group which is resistant to diffusion.

2. The color photographic material as in claim 1, wherein said compound represented by formula (A) is present in a layer other than the photosensitive silver halide emulsion layers.

3. The photographic material as in claim 1, wherein Cp is represented by the general formulae (Cp-1), (Cp-2), (Cp-3), (Cp-4), (Cp-5), (Cp-6), (Cp-7) or (Cp-8)

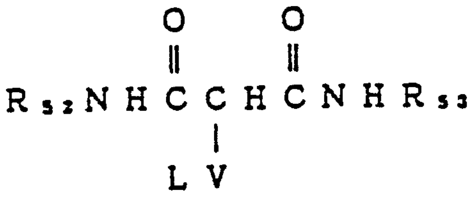
General formula (Cp-1)



$$R_{51}\overset{O}{\overset{\|}{C}}\underset{\underset{LV}{|}}{C}H\overset{O}{\overset{\|}{C}}NH-R_{52}$$

(Cp-1)

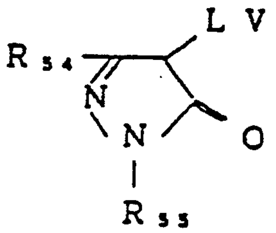
General formula (Cp-2)



$$R_{52}NH\overset{O}{\overset{\|}{C}}\underset{\underset{LV}{|}}{C}H\overset{O}{\overset{\|}{C}}NHR_{53}$$

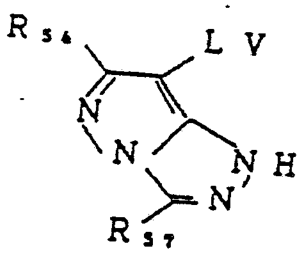
(Cp-2)

General formula (Cp-3)



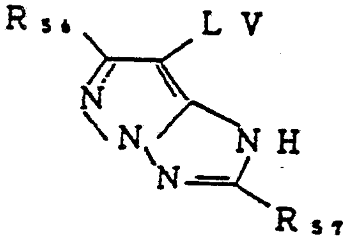
(Cp-3)

General formula (Cp-4)



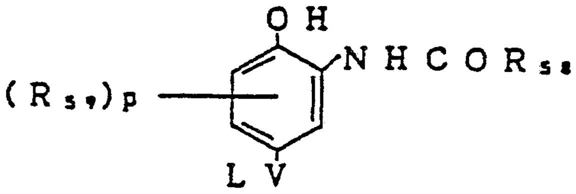
(Cp-4)

General formula (Cp-5)



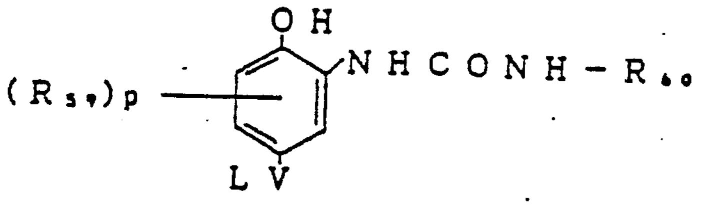
(Cp-5)

General formula (Cp-6)



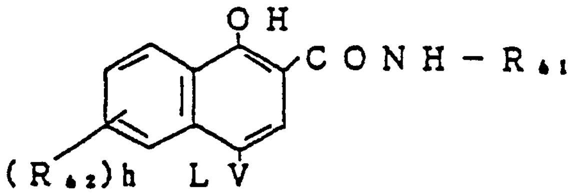
(Cp-6)

General formula (Cp-7)



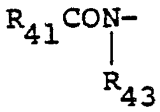
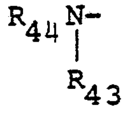
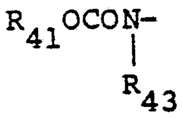
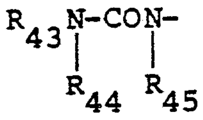
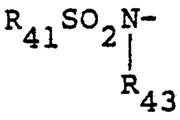
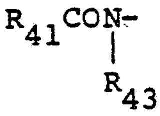
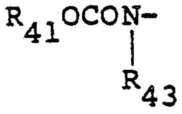
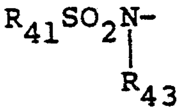
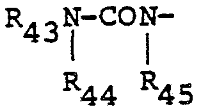
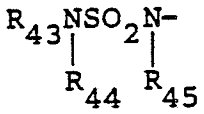
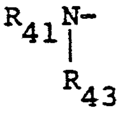
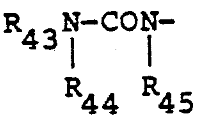
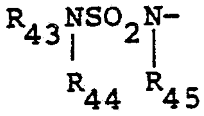
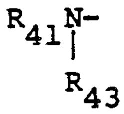
(Cp-7)

General formula (Cp-8)



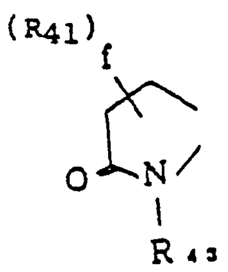
(Cp-8)

wherein in formula (Cp-1) at least one of R_{51} and R_{52}, in formula (Cp-2), at least one of R_{52} and R_{53}; in formula (Cp-3) at least one of R_{54} and R_{55}; in formula (Cp-4) at least one of R_{56} and R_{57}; in formula (Cp-5) at least one of R_{56} and R_{57}; in formula (Cp-6) at least one of R_{58} and R_{59}; in formula (Cp-7) at least one of R_{59} and R_{60} and in formula (Cp-8) at least one of R_{61} and R_{62} are a linking group with the Sol group or the Sol group itself; wherein R_{41} represents an aliphatic group, aromatic group or heterocyclic group, R_{42} represents an aromatic group or a heterocyclic group; R_{43}, R_{44} and R_{45} represent hydrogen atoms, aliphatic groups, aromatic groups or heterocyclic groups; R_{51} has the same significance as R_{41}; R_{52} and R_{53} both have the same significance as R_{42}; R_{54} has the same significance as R_{41}, an $R_{41}CO\underset{R_{43}}{\underset{|}{N}}-$ group, an $R_{41}\underset{R_{43}}{\underset{|}{N}}-$ group, and $R_{41}SO_2\underset{R_{43}}{\underset{|}{N}}-$ group, an $R_{41}S-$ group, an $R_{43}O-$ group, an $R_{45}\underset{R_{43}}{\underset{|}{N}}-CO\underset{R_{44}}{\underset{|}{N}}-$ group, an $R_{43}OOC-$ group, an $R_{44}\underset{R_{43}}{\underset{|}{N}}CO-$ group or an $N\equiv C$-group; R_{55} has the same significance as R_{41}; R_{56} and R_{57} each has the same significance as the R_{43} groups, $R_{41}S$-group, $R_{43}O$-groups,

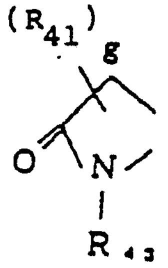

$R_{41}CO\underset{R_{43}}{N}-$ groups, 
$R_{44}\underset{R_{43}}{N}-$ groups, 
$R_{41}OCO\underset{R_{43}}{N}-$ groups, 
$R_{43}\underset{R_{44}}{N}-CO\underset{R_{45}}{N}-$ groups or 
$R_{41}SO_2\underset{R_{43}}{N}-$ groups; R_{58} has the same significance as R_{41}; R_{59} has the same significance as R_{41}, an 
$R_{41}CO\underset{R_{43}}{N}-$ group, an 
$R_{41}OCO\underset{R_{43}}{N}-$ group, an 
$R_{41}SO_2\underset{R_{43}}{N}-$ group, an 
$R_{43}\underset{R_{44}}{N}-CO\underset{R_{45}}{N}-$ group, an 
$R_{43}\underset{R_{44}}{N}SO_2\underset{R_{45}}{N}-$ group, an R_{41}O-group, an R_{41}S-group, a halogen atom or an 
$R_{41}\underset{R_{43}}{N}-$ group; p is a number of value 0 to 3 provided that when p is 2 or more the plurality of R_{59} groups may be the same or different substituent groups; wherein the R_{59} groups may be divalent groups which are joined to form a ring structure; wherein R_{60} has the same significance as R_{41}; R_{61} has the same significance as R_{41}; R_{62} has the same significance as R_{41}, an R_{41}CONH-group, and R_{41}OCONH-group, an $R_{41}SO_2$NH-group, an 
$R_{43}\underset{R_{44}}{N}-CO\underset{R_{45}}{N}-$ group, an 
$R_{43}\underset{R_{44}}{N}SO_2\underset{R_{45}}{N}-$ group, an R_{43}O-group, a halogen atom or an 
$R_{41}\underset{R_{43}}{N}-$ group; wherein h represents an integer of value 0 to 4 provided that in cases where there is a plurality of R_{62} groups these groups may be the same or different; wherein said aliphatic groups above are saturated or unsaturated, linear chain, branched chain or ring, substituted or unsubstituted aliphatic or cyclic hydrocarbon groups which have from 1 to 20 carbon atoms; and wherein said aromatic groups above have from 6 to 20 carbon atoms.

4. The color photographic materials as in Claim 3, wherein the combined substituents R_{51}, R_{52}, R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{59}, R_{60}, R_{61} and R_{62} present on any single molecule of the compound represented by formula (A) have not more than a total of 15 carbon atoms.

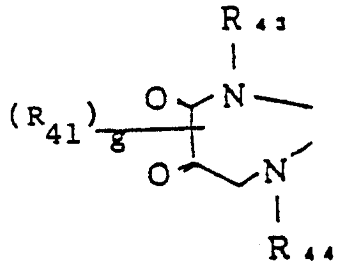
5. A color photographic material as in Claim 3, wherein said divalent groups which are joined to form a ring structure are represented by



group,



group or a



group.

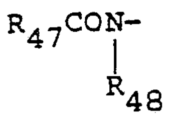
wherein f represents an integer of value 0 to 4 and g represents an integer of value 0 to 2.

6. The color photographic material as in Claim 3, wherein said aliphatic groups are selected from the group consisting of a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a ter-butyl group, an iso-butyl group, a tert-amyl group, a hexyl group, a cyclohexyl group, a 2-ethylhexyl group, an octyl group, a 1,1,3,3-tetramethylbutyl group, a decyl group, and said aromatic groups are selected from the group consisting of substituted or unsubstituted phenyl groups.

7. The color photographic material as in Claim 3, wherein said heterocyclic groups are selected from the group consisting of 3-to 8-membered substituted or unsubstituted heterocyclic groups wherein the hetero atoms are selected from the group consisting of nitrogen, oxygen and sulfur atoms and which groups may have from 1 to 12 carbon atoms.

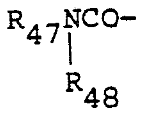
8. The color photographic material as in Claim 7, wherein said heterocyclic groups are selected from the group consisting of a 2-pyridyl group, a 4-pyridyl group, a 2-thienyl group, a 2-furyl group, a 2-imidazolyl group, a pyrazinyl group, a 2-pyrimidinyl group, a 1-imidazolyl group, a 1-indolyl group, a phthalimido group, a 1,3,4-thiadiazol-2-yl group, a benzoxazol-2-yl group, a 2-quinolyl group, a 2,4-dioxo-1,3-imidazolidin-5-yl group, a 2,4-dioxo-1,3-imidazolidin-3-yl group, a succinimido group, a 1,2,4-triazol-2-yl group and a 1-pyrazolyl group.

9. The color photographic material as in Claim 3, wherein said substituents for said aliphatic groups, aromatic groups and heterocyclic groups are selected from the group consisting of halogen atoms, $R_{47}O$-groups, $R_{46}S$ groups



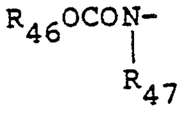
$R_{47}CO\underset{R_{48}}{\underset{|}{N}}-$

groups,



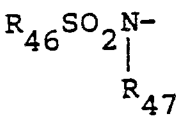
$R_{47}\underset{R_{48}}{\underset{|}{N}}CO-$

groups,



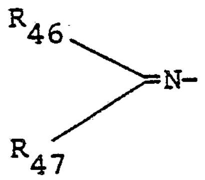
$R_{46}OCO\underset{R_{47}}{\underset{|}{N}}-$

groups,

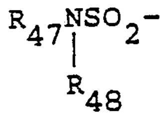


$R_{46}SO_2\underset{R_{47}}{\underset{|}{N}}-$

groups,

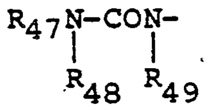


groups,



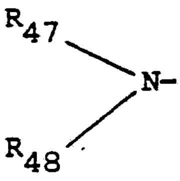
$R_{47}\underset{R_{48}}{\underset{|}{N}}SO_2-$

groups, $R_{46}SO_2$-groups, $R_{47}OCO$-groups,



$R_{47}\underset{R_{48}}{\underset{|}{N}}-CO\underset{R_{49}}{\underset{|}{N}}-$

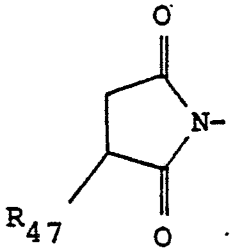
groups,



groups,

$$\overset{\mathrm{O}}{\|}$$

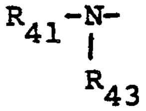
groups which have the same significance as R_{46},



groups,

$R_{46}COO$-groups, $R_{47}OSO_2$-groups, cyano groups and nitro groups, wherein R_{46} represents an aliphatic group, an aromatic group or a heterocyclic group and R_{47}, R_{48} and R_{49} and which may be the same or different each represents an aliphatic group, an aromatic group, a heterocyclic group or a hydrogen atom.

10. The color photographic material as in Claim 3, wherein R_{51} is an aliphatic group or an aromatic group, R_{52}, R_{53} and R_{55} are aromatic groups; R_{54} is a $R_{41}COHN$-group or a



$R_{41}-\underset{R_{43}}{\underset{|}{N}}-$

group; R_{56} and R_{57} each is an aliphatic group, a $R_{41}O$-group or a $R_{41}S$-group; R_{58} is an aliphatic group or an aromatic group; wherein in formula (Cp-6), R_{59} is a chlorine atom, an aliphatic group or an $R_{41}CONH$-group, p has a value of 0 to 2 and R_{60} is an aromatic group; wherein in formula (Cp-7), R_{59} is an $R_{41}COHN$-group and p is 0 to 2; wherein in formula (Cp-8), R_{61} is an aliphatic group or an aromatic group and h has a value of 0 or 1; and wherein R_{62} is an R_{41}OCONH-group, an R_{41}CONH-group or an $R_{41}SO_2HN$-group.

11. The color photographic material as in Claim 10, wherein the substitution position of the substituent groups in formula (Cp-8) is the 5-position of the naphthol ring.

12. The color photographic material as in Claim 3, wherein Sol is one or more groups selected from the group consisting of a hydroxyl group, a carboxylic acid group and salts thereof, a sulfinic acid group and salts thereof, a sulfonic acid group and salts thereof, an amino group, a phosphinic acid group and salts thereof, a phosphonic acid group and salts thereof, a sodium salt, a potassium salt and an ammonium salt.

13. The color photographic material as in Claim 1, wherein said compounds represented by formula (A) are present in an amount of from 1×10^{-7} to 1×10^{-2} mol per square meter.

14. The color photographic material as in Claim 1, wherein said compounds represented by formula (A) are present in an amount of from 1×10^{-6} to 3×10^{-3} mol per square meter.

15. The color photographic material as in Claim 1, wherein said compounds represented by formula (A) are present in an amount of from 1×10^{-5} to 3×10^{-3} mol per square meter.

16. The color photographic material as in Claim 1, wherein said compounds represented by formula (A) are present in a silver halide layer in an amount of from 1×10^{-4} to 1 mol per square meter.

17. The color photographic material as in Claim 1, wherein said compounds represented by formula (A) are present in a silver halide layer in an amount of from 3×10^{-4} to 3×10^{-1} mol per square meter.

18. The color photographic material as in Claim 1, wherein said compounds represented by formula (A) are present in a silver halide layer in an amount of from 1×10^{-3} to 1×10^{-1} mol per square meter.