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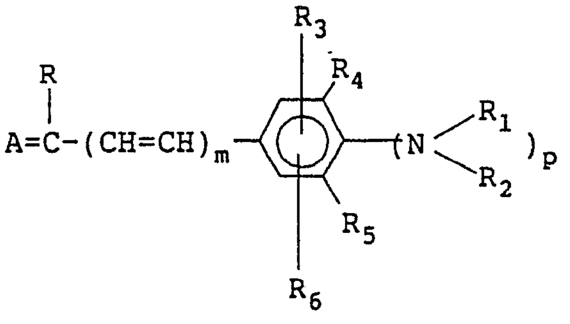
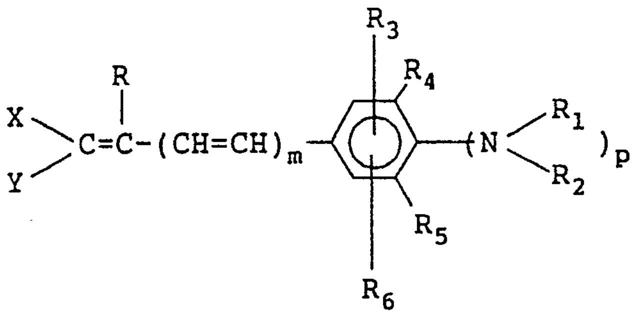
(54) Silver halide color reversal photographic photosensitive material.

(57) A silver halide color reversal photographic photosensitive material is disclosed comprising a support having thereon at least one red sensitive emulsion layer, at least one green sensitive emulsion layer and at least one blue sensitive emulsion layer, at least one hydrophilic colloid layer of said photographic photosensitive material containing a microcrystalline dispersion of at least one compound selected from the compounds represented by formulae (I), (II), (III), (IV), (V) and (VI), and at least one hydrophilic colloid layer of said photographic photosensitive material containing at least one compound represented by formula (VII):



(I)



(II)

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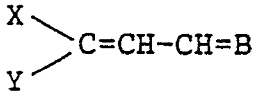
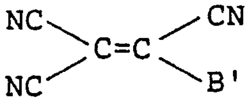
$$A=L_1-(L_2=L_3)_n-A' \qquad (III)$$

$$A=(L_1-L_2)_{2-q}=B \qquad (IV)$$



(V)



(VI)

wherein A and A′, which may be the same or different, each represents an acidic nucleus; B represents a basic nucleus; and X and Y, which may be the same or different, each represents an electron attractive group; R represents a hydrogen atom or an alkyl group; R_1 and R_2 each represent an alkyl group, an aryl group, an acyl group or a sulfonyl group, or R_1 and R_2 are joined together to form a five or six membered ring; R_3 and R_6 each represent a hydrogen atom, a hydroxy group, a carboxyl group, an alkyl group, an alkoxy group or a halogen atom; R_4 and R_5 each represent a hydrogen atom or a group of non-metal atoms joined together with R_1 and R_2, respectively, to form a five or six membered ring; L_1, L_2 and L_3 each represent a methine group; m represents 0 or I, n and q each represent 0, 1 or 2, and p represents 0 or 1, and when p is 0, R_3 represents a hydroxy group or a carboxyl group and R_4 and R_5 each represent a hydrogen atom; B′ represents a heterocyclic group containing a carboxyl group, a sulfamoyl group or a sulfonamido group;

said compound represented by formulae (I) to (VI) containing at least one dissociable group such taht the pKa value of the compound in a 1 : 1 by volume mixed solvent comprising water and ethanol is within the range of from 4 to 11:

$A\text{-}(Time)_t\text{-}Z$ (VII)

wherein A represents a redox parent nucleus which eliminate $-(Time)_t-Z$ by oxidation during photographic development processing; Time represents a timing group which is bonded to A with a sulfur atom, a nitrogen atom, an oxygen atom or a selenium atom; t represents an integer of value 0 or 1; and Z represents a development inhibitor group.

SILVER HALIDE COLOR REVERSAL PHOTOGRAPHIC PHOTOSENSITIVE MATERIAL

FIELD OF THE INVENTION

This invention concerns silver halide color reversal photographic photosensitive materials which having excellent sharpness and color reproduction properties and excellent de-silvering properties.

BACKGROUND OF THE INVENTION

Silver halide color reversal photographic photosensitive materials provide, upon exposure and development processing, a positive image for use in preparing printing originals, etc. In recent years in particular, there has been a demand for improved sharpness and graininess in printing originals to accomodate the higher magnifications used for enlargement of a smaller format, and there is also a demand for increased sharpness and better color reproduction properties.

Various proposals have been advanced to improve the image quality and color reproduction of silver halide color reversal photographic photosensitive materials by modifying the form of the silver halide (for example, by using a mono-disperse emulsion and/or tabular emulsion), by adjusting the halogen composition, and by adjusting the distribution of the halide ion, for example.

Sensitizing dyes have been developed and methods for the addition of dyes have been used, for example, for adjusting spectral sensitivities; however, there is a need for the development of additional useful techniques. In the case of color negative photosensitive materials, image quality and color reproduction, etc. have been improved using DIR couplers which release development inhibitors in the course of the color development process. However, with color reversal photosensitive materials the effect of the black and white development which is carried out at the beginning of the processing operation is critical, and the possibility of control using couplers is limited.

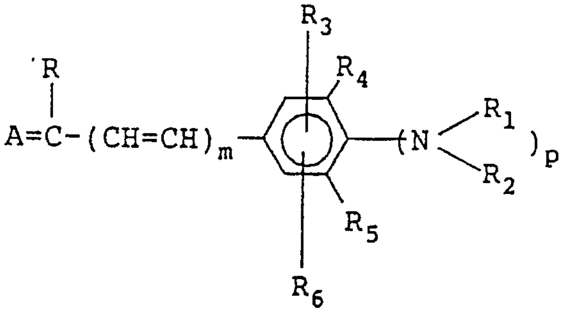
A known technique for improving the sharpness and color reproduction of silver halide color reversal photographic photosensitive materials using a black and white developer involves the use of DIR hydroquinones which release development inhibitors during development processing to thereby control the development (U.S. Patents 3,379,529 and 3,639,417, and JP-A-49-129536). (The term "JP-A" as used herein signifies an "unexamined published Japanese patent application".) However, although the use of DIR hydroquinones is useful for increasing picture quality and for improving color reproduction, the development inhibitors which are released retard de-silvering. Particularly, upon bleaching the developed silver and fixing, some developed silver (i.e., residual silver) remains in the sensitive material. Problems also arise with dark brown staining, and the usefulness of this method is therefore limited.

Furthermore, attempts have been made to replace the colloidal silver, namely, the yellow colloidal silver which is used in yellow filter layers and the black colloidal silver which is used in anti-halation layers, which colloidal silver tends to be left behind after processing with dyes, as a means of improving desilvering properties. For example, mordanting techniques with basic polymers and acidic dyes (U.S. Patents 2,548,562, 4,124,386 and 3,625,694) in which dissolution and wash-out into the processing bath occurs, and methods in which oil soluble dye which are decolorized by reaction with sulfite ion present in the processing bath (U.S. Patent 4,420,555, JP-A-61-204630 and JP-A-62-222248) have been proposed. However, these methods are disadvantageous in that the diffusion properties of the dyes are not suppressed, and thus the sensitivity of other layers is reduced, and problems may arise with color staining of the white base parts if the dyes are not completely decolorized. Furthermore, methods in which dyes are added in the form of solid dispersions or microcrystalline dispersions have been proposed (WO 88/04794, or JP-A-56-12639, JP-A-55-155350, JP-A-55-155351 and European Patent 15,601), but when these methods are applied to color reversal photographic photosensitive materials, the development activity promoting effect of the colloidal silver is lost and problems inevitably arise with image quality and color reproduction.

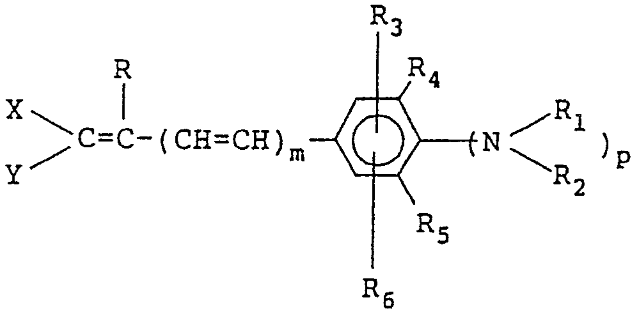
SUMMARY OF THE INVENTION

An object of the present invention is to provide a silver halide color reversal photographic photosensitive material having excellent sharpness and color reproducibility and which also have excellent desilvering properties.

The above objective has been achieved by providing a silver halide color reversal photographic photosensitive material comprising a support having thereon at least one red sensitive emulsion layer, at least one green sensitive emulsion layer and at least one blue sensitive emulsion layer, wherein at least one hydrophilic colloid layer of said photographic photosensitive material contains a microcrystalline dispersion of at least one compound selected from the group of compounds represented by formulae (I), (II), (III), (IV), (V) and (VI) and at least one hydrophilic colloid layer of said photographic photosensitive material contains at least one compound represented by formula (VII):



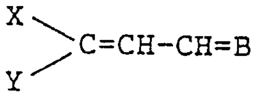
(I)



(II)

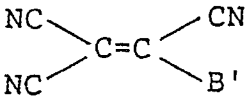
$$A=L_1-(L_2=L_3)_n-A' \qquad \text{(III)}$$

$$A=(L_1-L_2)_{2-q}=B \qquad \text{(IV)}$$



$$\begin{matrix}X\\Y\end{matrix}\!>\!C=CH-CH=B$$

(V)



$$\begin{matrix}NC\\NC\end{matrix}\!>\!C=C\!<\!\begin{matrix}CN\\B'\end{matrix}$$

(VI)

wherein A and A′ which may be the same or different, each represents an acidic nucleus, B represents a basic nucleus, and X and Y, which may be the same or different, each represents an electron attractive group. R represents a hydrogen atom or an alkyl group, R_1 and R_2 each represent an alkyl group, an aryl group, an acyl group or a sulfonyl group, or R_1 and R_2 are joined together to form a five or six membered ring. R_3 and R_6 each represent a hydrogen atom, a hydroxy group, a carboxyl group, an alkyl group, an alkoxy group or a halogen atom, R_4 and R_5 each represent a hydrogen atom or a group of non-metal atoms joined together with R_1 and R_2, or R_2 respectively, to form a five or six membered ring. L_1, L_2 and L_3 each represent a methine group. moreover, m represents 0 or 1, n and q each represent 0, 1 or 2, and p represents 0 or 1, and when p is 0, R_3 represents a hydroxy group or a carboxyl group and R_4 and R_5 each represent a hydrogen atom. B′ represents a heterocyclic group containing a carboxyl group, a sulfamoyl group or a sulfonamido group.

Furthermore, the compound represented by formulae (I) to (VI) contains at least one dissociable group such that the pKa value of the compound in a 1 : 1 by volume mixed solvent comprising water and ethanol is within the range of from 4 to 11.

$A\text{-}(\mathrm{Time})_t\text{-}Z$ (VII)

In formula (VII), A represents a redox parent nucleus which eliminates $\text{-}(\mathrm{Time})_t\text{-}Z$ by oxidation during photographic development processing, Time represents a timing group which is bonded to A with a sulfur atom, a nitrogen atom, an oxygen atom or a selenium atom, t represents an integer of value 0 or 1, and Z represents a development inhibitor group.

DETAILED DESCRIPTION OF THE INVENTION

The hydrophilic colloid layer of the present invention containing a microcrystalline dye is described below.

The dye contained in the hydrophilic colloid layer is at least one compound selected from among those compounds represented by formulae (I), (II), (III), (IV), (V) and (VI) described below.

First, the compounds represented by the formulae (I) to (VI) are described in detail.

The acidic nucleus represented by each of A and A′ preferably is a 2-pyrazolin-5-one, rhodanine, hydantoin, thiohydantoin, 2,4-oxazolidindione, isooxazolidinone, barbituric acid, thiobarbituric acid, indandione, pyrazolopyridine or hydroxypyridine nucleus.

The basic nucleus represented by B preferably is a pyridine, quinoline, indolenine, oxazole, benzoxazole, naphthoxazole or pyrrole nucleus.

Examples of the heterocyclic ring represented by B′ include a pyrrole, indole, thiophene, furan, imidazole, pyrazole, indolidine, quinoline, carbazole, phenothiazine, phenoxazine, indoline, thiazole, pyridine, pyridazine, thiadiazine, pyran, thiopyran, oxadiazole, benzoquinolidine, thiadiazole, pyrolothiazole, pyrolopyridazine and tetrazole ring.

The group having a dissociable group, e.g., proton such that the pKa (acid dissociation constant) of the compound in a 1 : 1 by volume mixture of water and methanol is within the range from 4 to 11 is not subject to any particular limitation with respect to the position onto which the group is substituted into the molecule, provided that the dye molecule is substantially water insoluble, preferably 1 x 10^{-2} g or less of solubility based on 100 g of water, and more preferably 1 x 10^{-3} g or less based on 100 g of water, at pH 6 or below pH 6 and substantially water soluble, preferably 0.5 g or more of solubility based on 100 g of water, and more preferably 1 g or more based on 100 g of water, at pH 8 or above pH 8. The group having a dissociable proton is preferably a carboxyl group, a sulfamoyl group, a sulfonamido group or a hydroxy group, and most desirably a carboxyl group. The dissociable group can be substituted directly onto the dye molecule and can also be substituted via a divalent linking group (for example, an alkylene group or a phenylene group). Examples of the group having a dissociable proton linked via a divalent linking group include 4-carboxyphenyl, 2-methyl-3-carboxyphenyl, 2,4-dicarboxyphenyl, 3,5-dicarboxyphenyl, 3-carboxyphenyl, 2,5-dicarboxyphenyl, 3-ethylsulfamoylphenyl, 4-phenylsulfamoylphenyl, 2-carboxyphenyl, 2,4,6-trihydroxyphenyl, 3-benzenesulfonamidophenyl, 4-(p-thiamibenzenesulfonamido)phenyl (sic), 3-hydroxyphenyl, 2-hydroxyphenyl, 4-hydroxyphenyl, 2-hydroxy-4-carboxyphenyl, 3-methoxy-4-carboxyphenyl, 2-methyl-4-phenylsulfamoylphenyl, 4-carboxybenzyl, 2-carboxybenzyl, 3-sulfamoylphenyl, 4-sulfamoylphenyl, 2,5-disulfamoylphenyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 4-carboxybutyl and 8-carboxyoctyl.

The alkyl groups represented by R, R_3 or R_6 are preferably alkyl groups having from 1 to 10 carbon atoms, for example methyl, ethyl, n-propyl, iso-amyl or n-octyl groups.

The alkyl groups represented by R_1 and R_2 are preferably alkyl groups having from 1 to 20 carbon atoms (for example, methyl, ethyl, n-propyl, n-butyl, n-octyl, n-octadecyl, iso-butyl, iso-propyl), and these groups may be substituted with substituent groups including, for example, halogen atoms such as chlorine and bromine, nitro, cyano, hydroxy and carboxy groups, alkoxy groups (for example, methoxy, ethoxy), alkoxycarbonyl groups (for example, methoxycarbonyl, iso-propoxycarbonyl), aryloxy groups (for example, phenoxy), phenyl groups, amido groups (for example, acetylamino, methanesulfonamido), carbamoyl groups (for example, methylcarbamoyl, ethylcarbamoyl) and sulfamoyl groups (for example, methylsulfamoyl, phenylsulfamoyl).

The aryl groups represented by R_1 or R_2 are preferably phenyl groups or naphthyl groups, which may be substituted with substituent groups including, for example, the groups indicated as substituent groups for the alkyl groups represented by R_1 and R_2, and alkyl groups (for example, methyl, ethyl)].

The acyl groups represented by R_1 or R_2 preferably have from 2 to 10 carbon atoms, and examples include the acetyl, propionyl, n-octanoyl, n-decanoyl, iso-butanoyl and benzoyl groups. Examples of the alkylsulfonyl groups and arylsulfonyl groups represented by R_1 or R_2 include the methanesulfonyl, ethanesulfonyl, n-butanesulfonyl, n-octanesulfonyl, benzenesulfonyl, p-toluenesulfonyl and o-carboxybenzenesulfonyl groups.

The alkoxy groups represented by R_3 and R_6 preferably have from 1 to 10 carbon atoms, and examples include the methoxy, ethoxy, n-butoxy, n-octyloxy, 2-ethylhexyloxy, iso-propoxy and iso-butoxy groups. The halogen atoms represented by R_3 or R_6 can be chlorine, bromine or fluorine atoms.

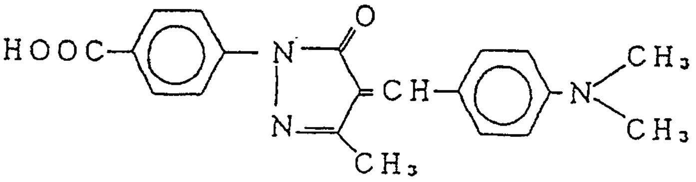
The 5-membered and 6-membered rings formed by joining together R_1 and R_2 include, for example, piperidine ring, morpholine ring, pyrrolidine ring, etc.

The rings formed by the joining together of R_1 and R_4, or R_2 and R_5, include, for example, julolidine rings, indoline ring, tetrahydroquinoline ring, etc.

The methine groups represented by L_1, L_2 and L_3 may be substituted with substituent groups including, for example, methyl, ethyl, cyano, phenyl, chlorine atom, hydroxypropyl. The electron attractive group represented by X or Y may be the same or different, each representing a cyano group, a carboxyl group, an alkylcarbonyl group (which may be a substituted alkylcarbonyl group, for example acetyl, propionyl, heptanoyl, dodecanoyl, hexadecanoyl, 1-oxo-7-chloroheptyl), an arylcarbonyl group (which may be a substituted arylcarbonyl group, for example benzoyl, 4-ethoxycarbonylbenzoyl, 3-chlorobenzoyl), an alkoxycarbonyl group (which may be a substituted alkoxycarbonyl group, for example methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl, t-amyloxycarbonyl, hexyloxycarbonyl, 2-ethylhexyloxycarbonyl, octyloxycarbonyl, decyloxycarbonyl, dodecyloxycarbonyl, hexadecyloxycarbonyl, octadecyloxycarbonyl, 2-butoxyethoxycarbonyl, 2-methylsulfonylethoxycarbonyl, 2-cyanoethoxycarbonyl, 2-(2-chloroethoxy)-ethoxycarbonyl, 2-[2-(2-chloroethoxy)ethoxy]ethoxycarbonyl), an aryloxycarbonyl group (which may be a substituted aryloxycarbonyl group, for example phenoxycarbonyl, 3-ethylphenoxycarbonyl, 4-ethylphehoxycarbonyl, 4-fluorophenoxycarbonyl, 4-nitrophenoxycarbonyl, 4-methoxyphenoxycarbonyl, 2,4-di(tert-amyl) phenoxycarbonyl), a carbamoyl group (which may be a substituted carbamoyl group, for example carbamoyl, ethylcarbamoyl, dodecylcarbamoyl, phenylcarbamoyl, 4-methoxyphenylcarbamoyl, 2-bromophenylcarbamoyl, 4-chlorophenylcarbamoyl, 4-ethoxycarbonylphenylcarbamoyl, 4-propylsulfonylphenylcarbamoyl, 4-cyanophenylcarbamoyl, 3-methylphenylcarbamoyl, 4-hexyloxyphenylcarbamoyl, 2,4-di(tert-amyl)-phenylcarbamoyl, 2-chloro-3-(dodecyloxycarbamoyl)phenylcarbamoyl, 3-(hexyloxycarbonyl)-phenylcarbamoyl), a sulfonyl group (for example, methylsulfonyl, phenylsulfonyl), or a sulfamoyl group (which may be a substituted sulfamoyl group, for example, sulfamoyl, methylsulfamoyl).

Useful examples of dyes for use in the present invention are provided below.

(I-1)



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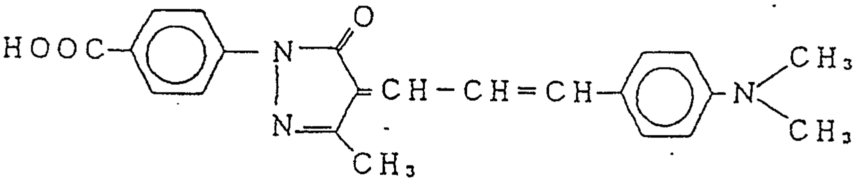

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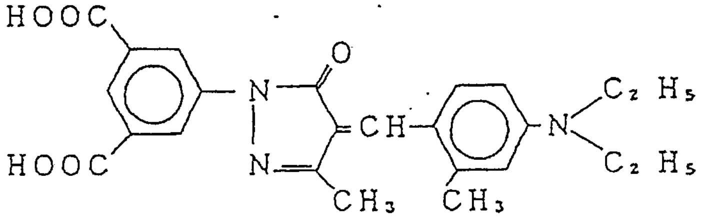
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HOOC
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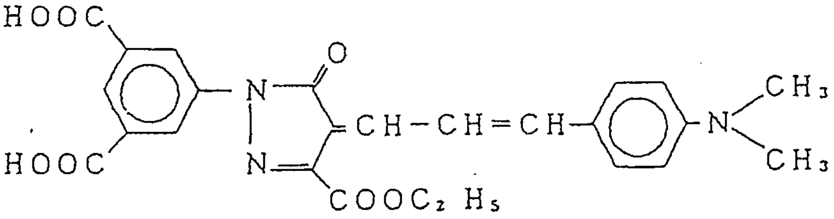
N
O
CH
CH₃
CH₃
N
C₂ H₅
C₂ H₅

(I-4)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HOOC
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N
O
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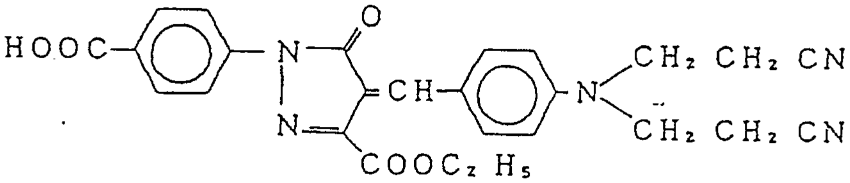
COOC₂ H₅
N
CH₃
CH₃

(I-5)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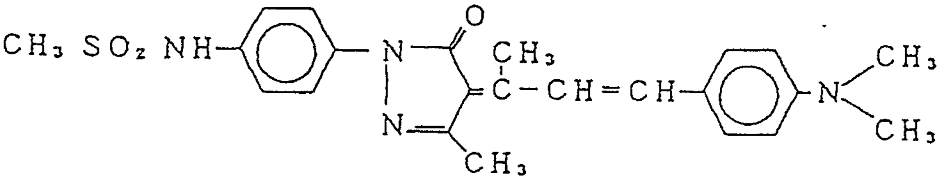
N
O
CH
COOC₂ H₅
N
CH₂ CH₂ CN
CH₂ CH₂ CN

(I-6)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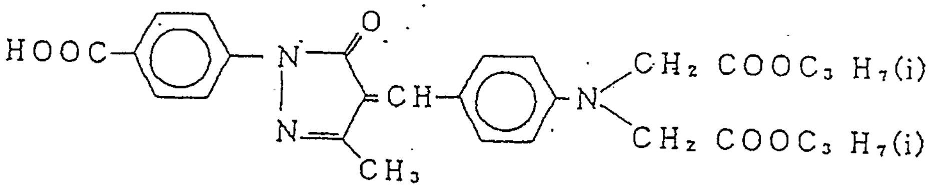
N
N
O
CH₃
C−CH=CH
CH₃
N
CH₃
CH₃

(I-7)



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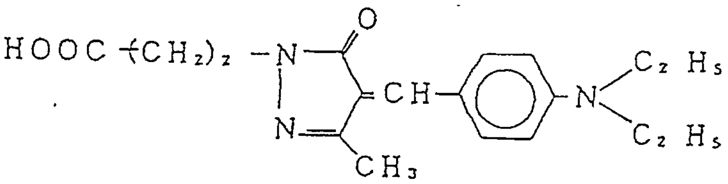

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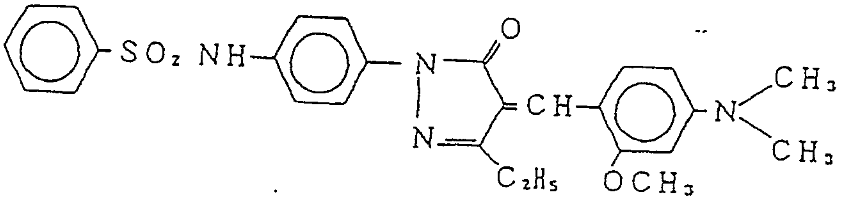

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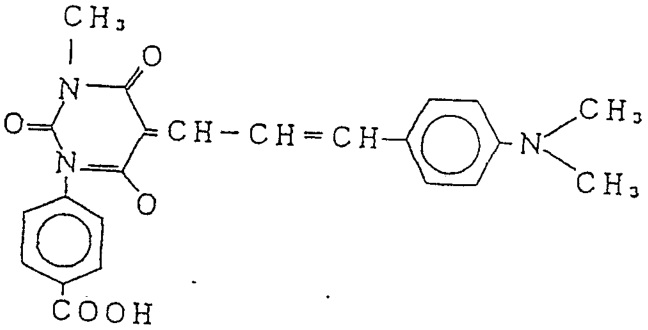

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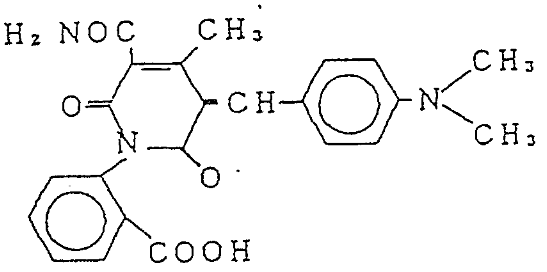

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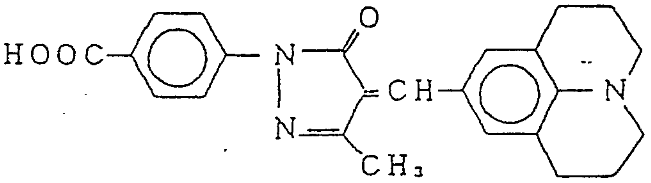

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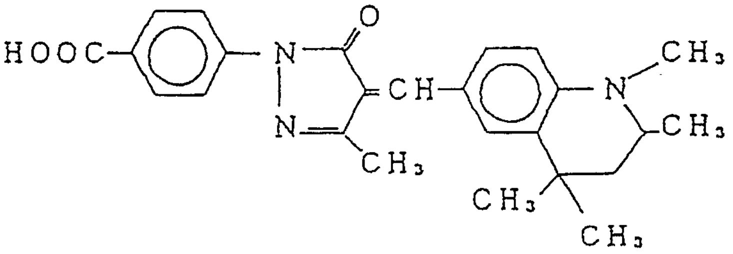

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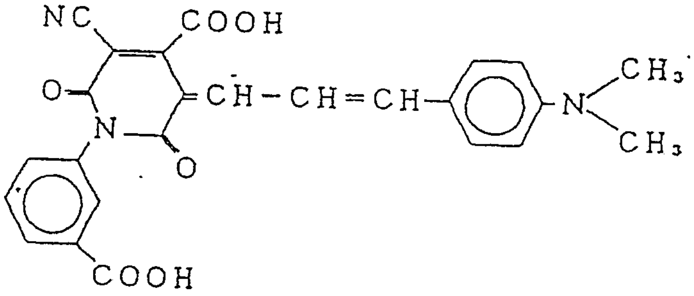

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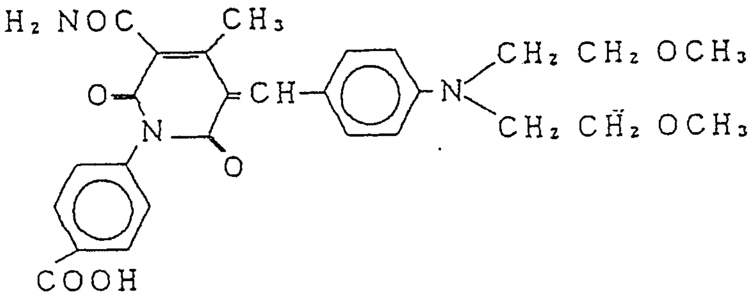

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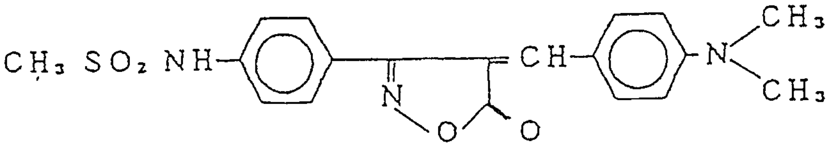

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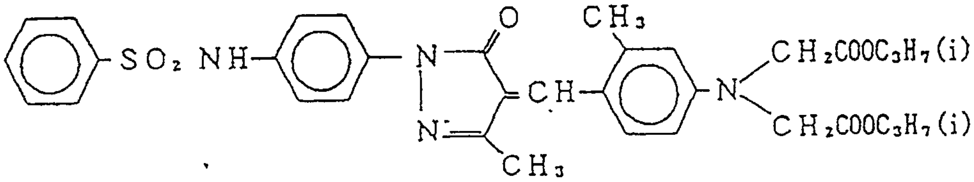

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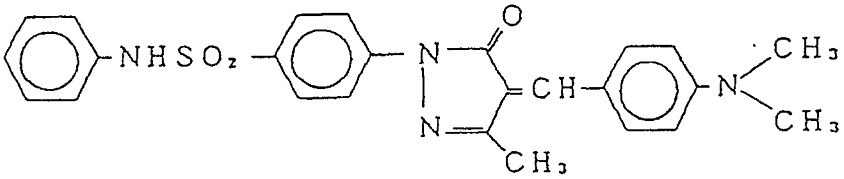

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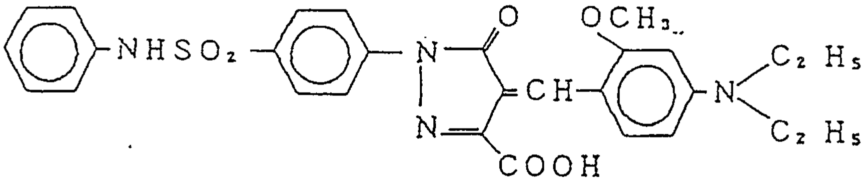

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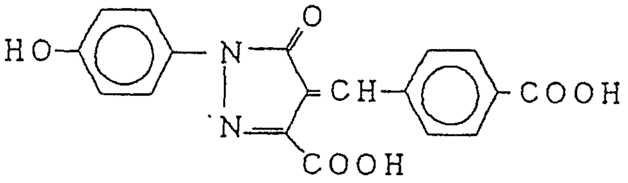

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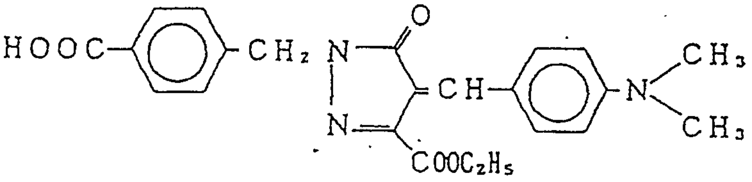

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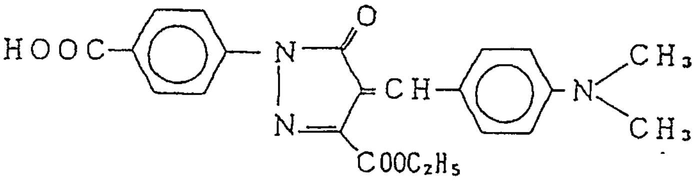

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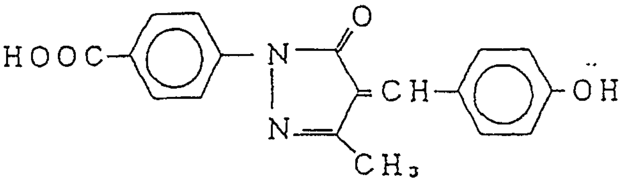

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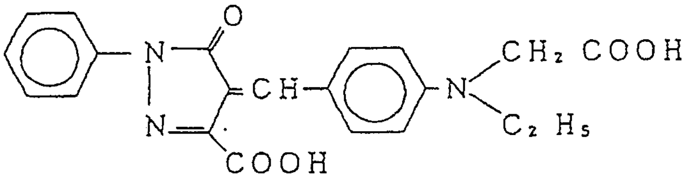

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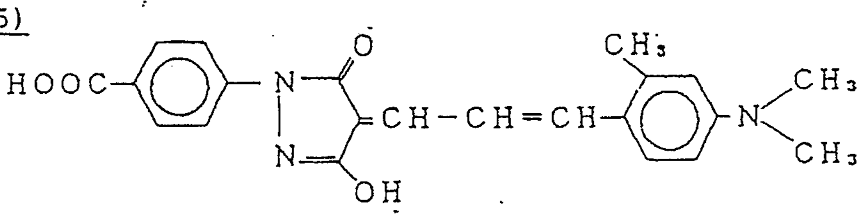

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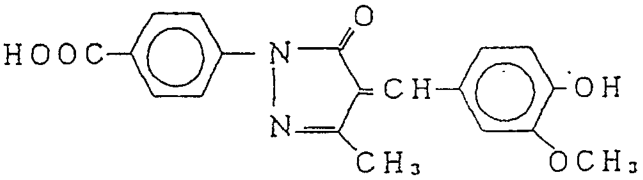

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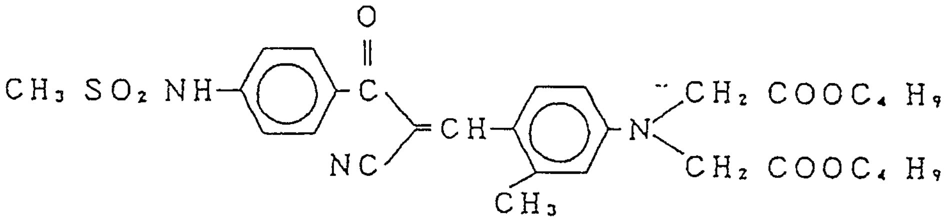

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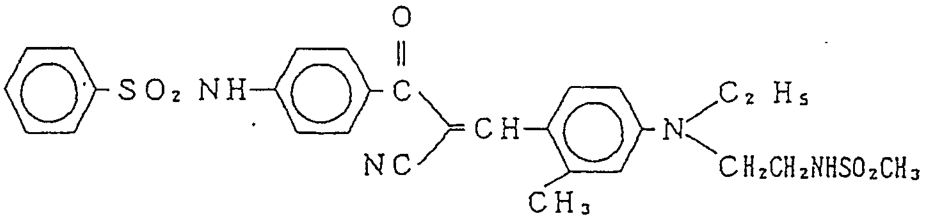

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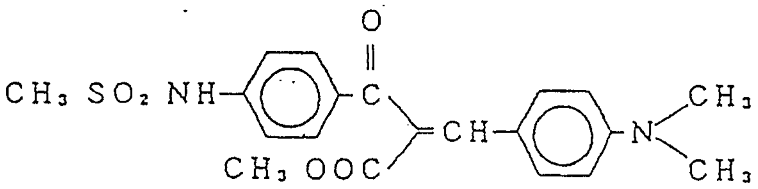

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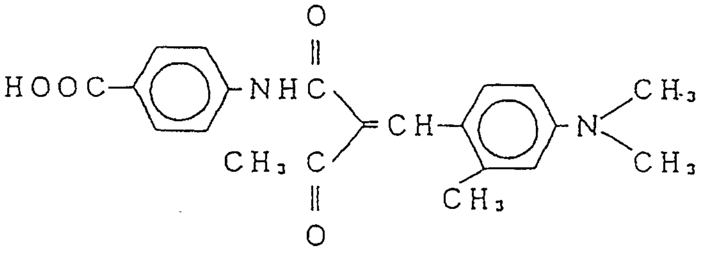

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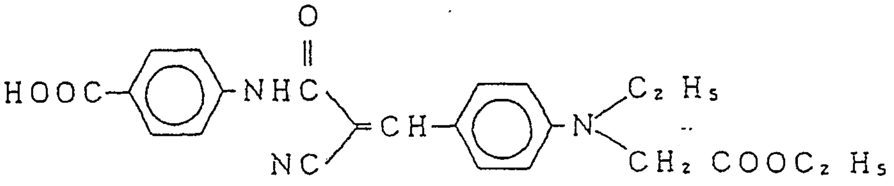

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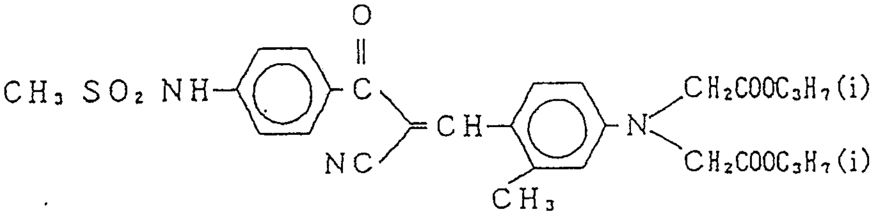

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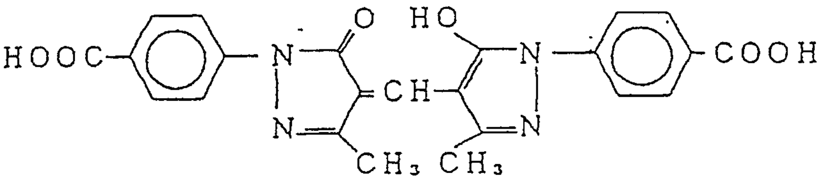

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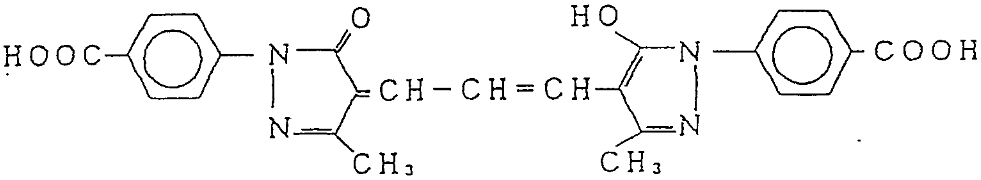

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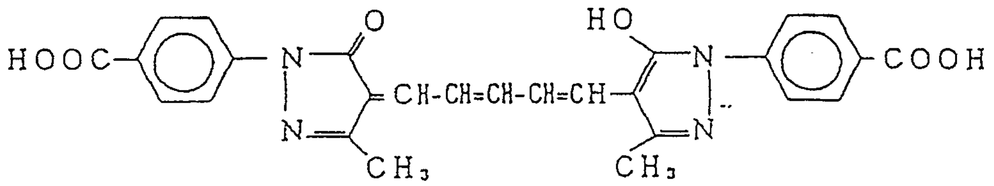

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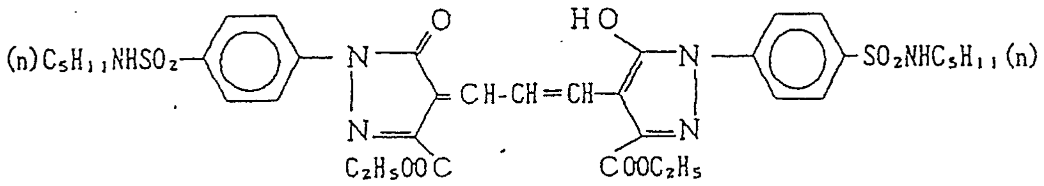

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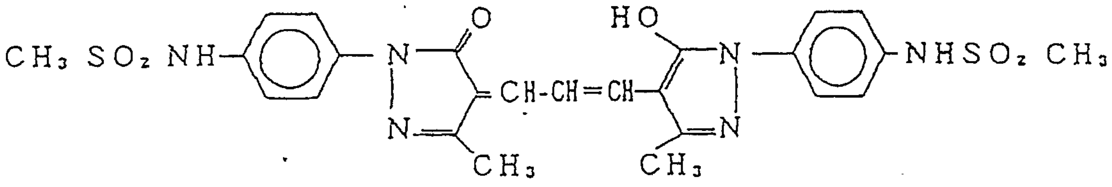

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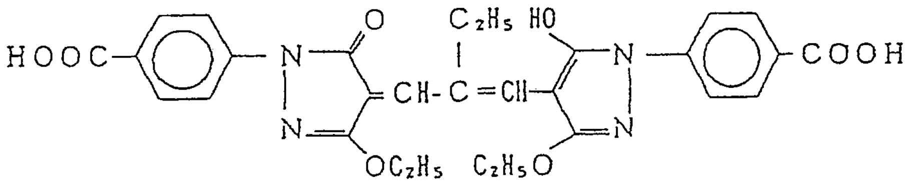

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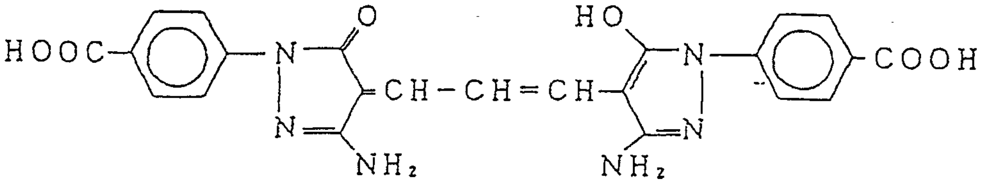

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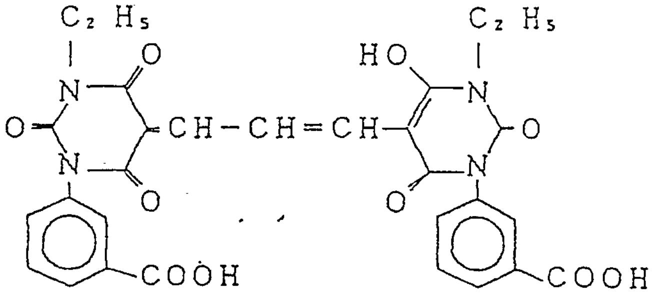

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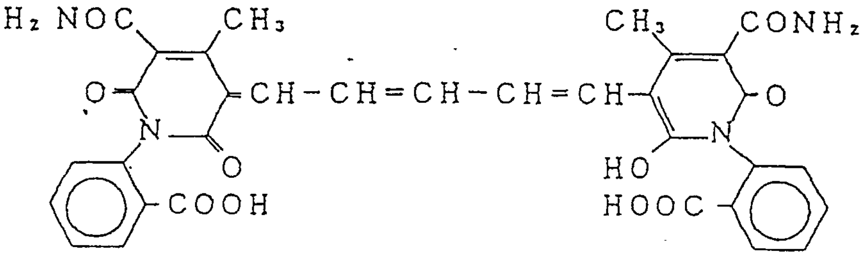

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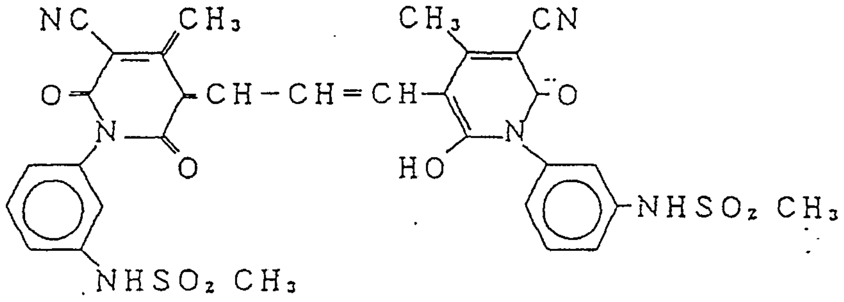

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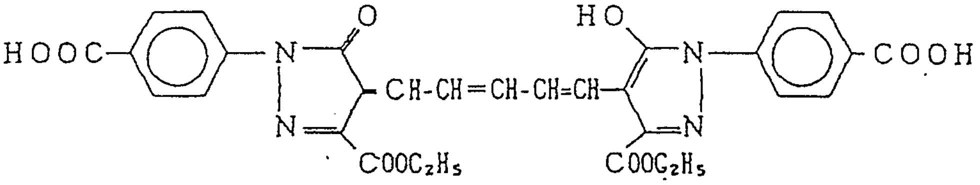

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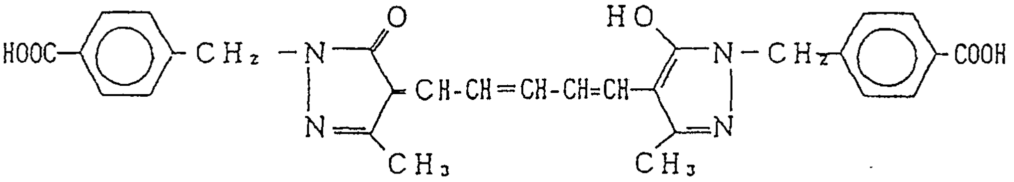

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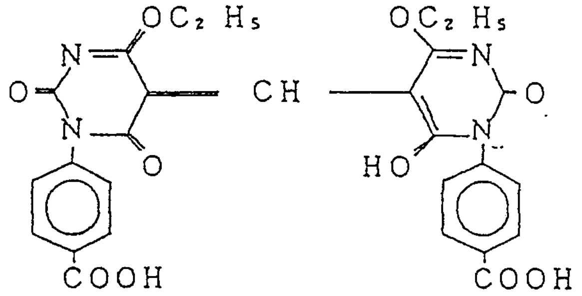

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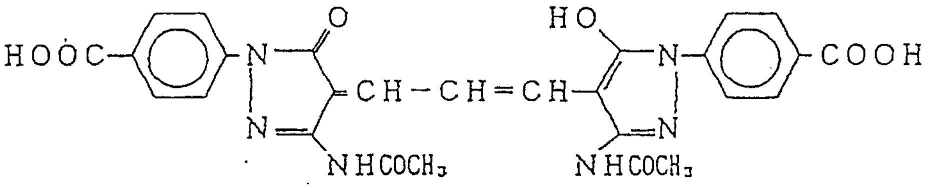

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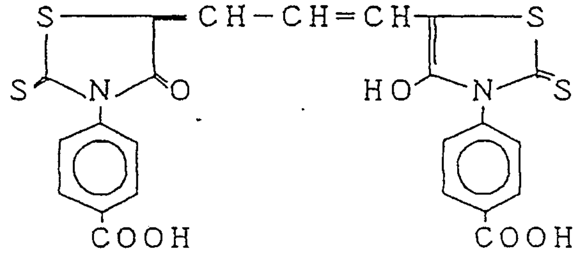

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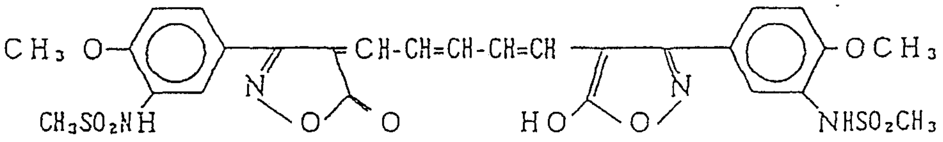

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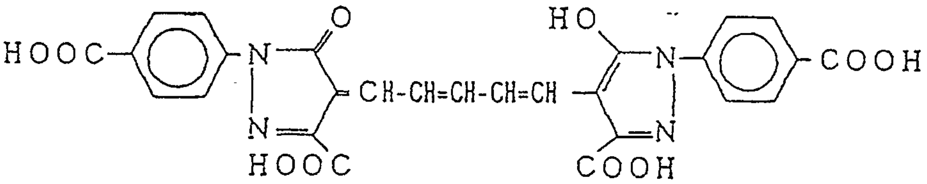

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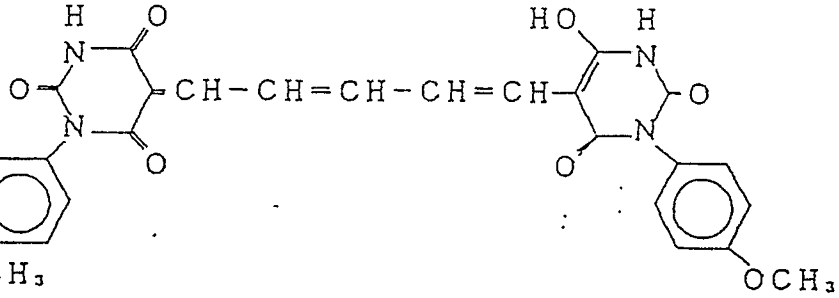

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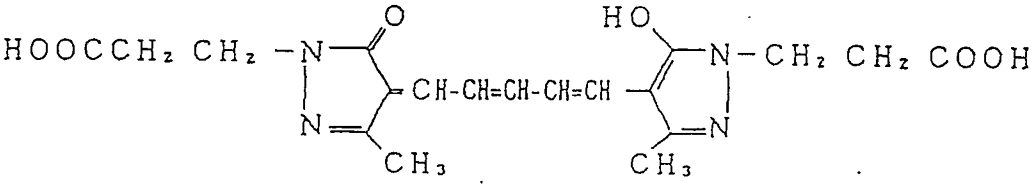

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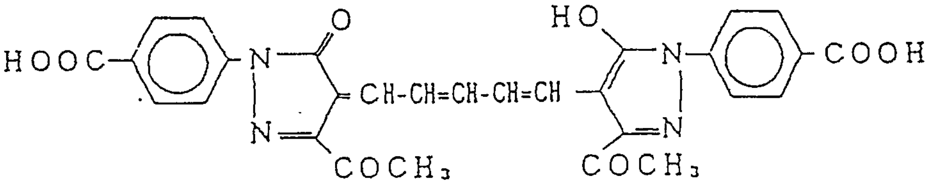

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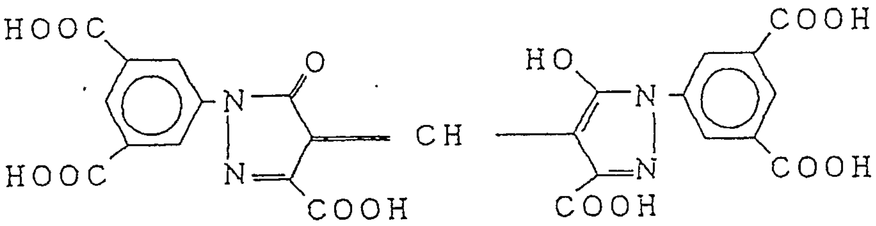

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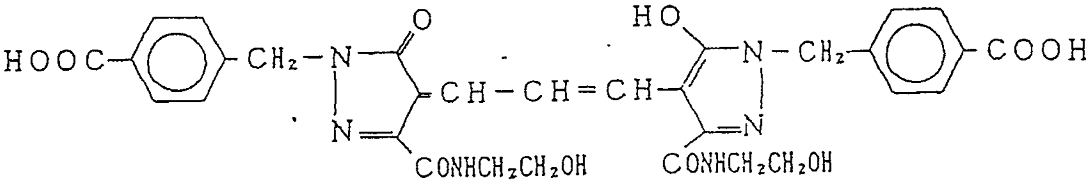

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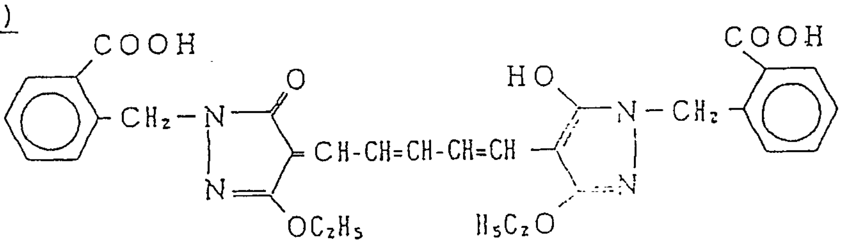

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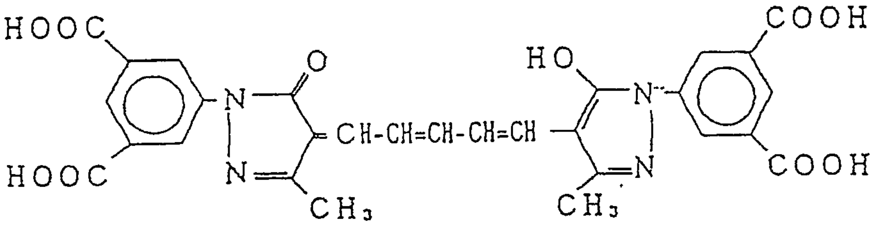

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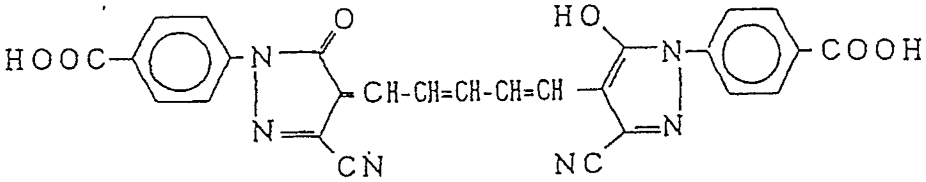

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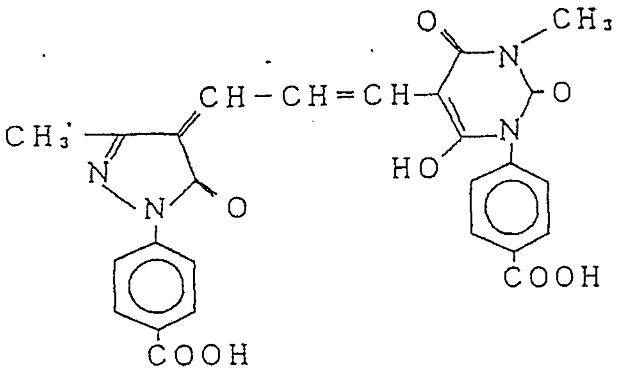

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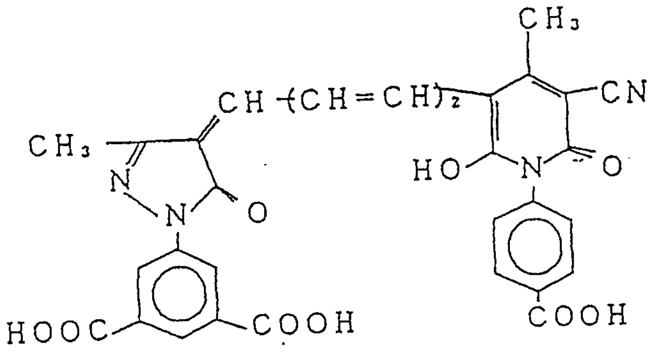

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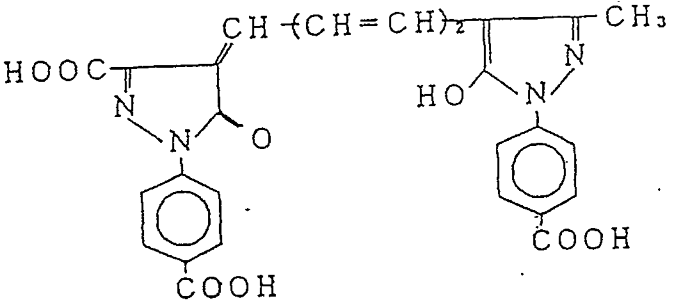

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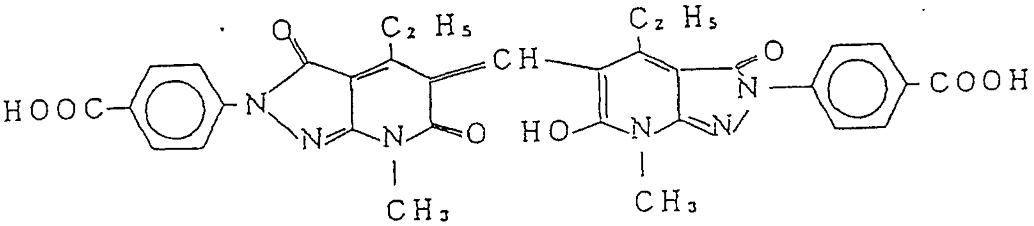

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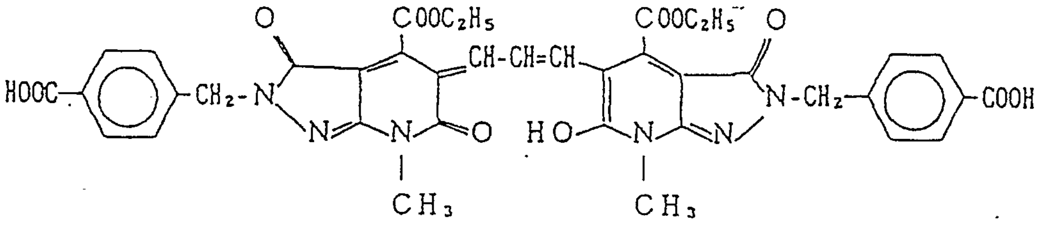

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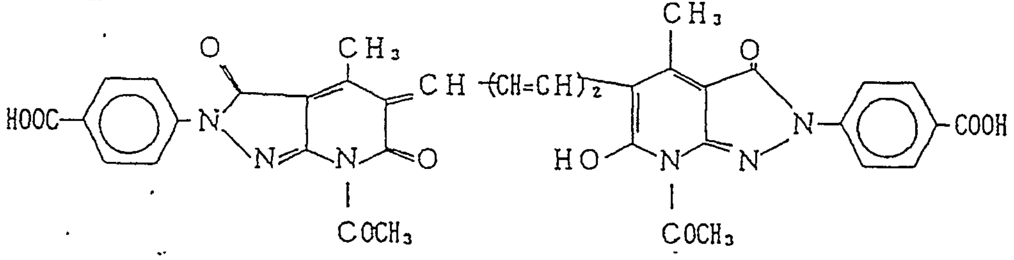

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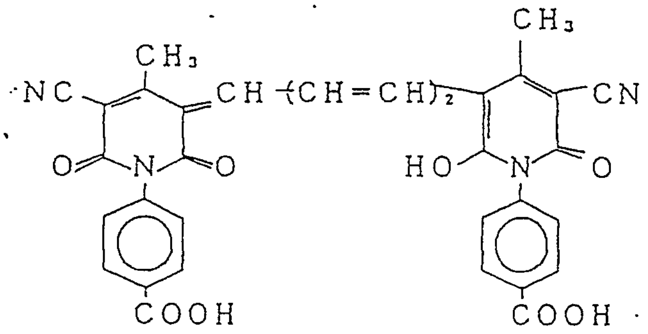

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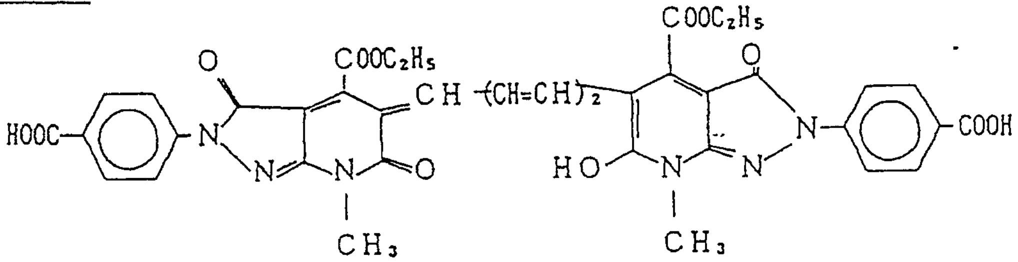

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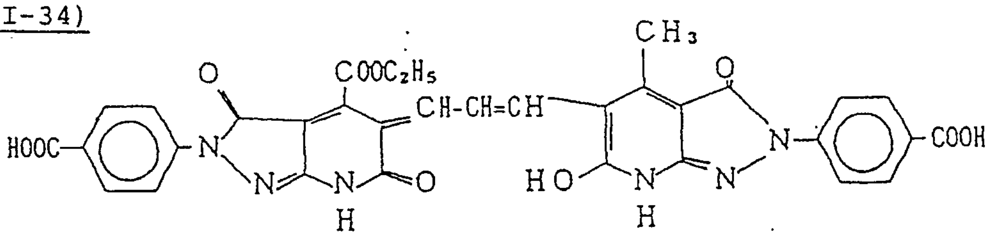

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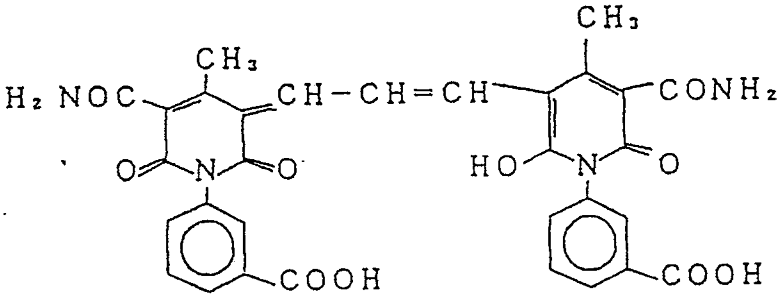

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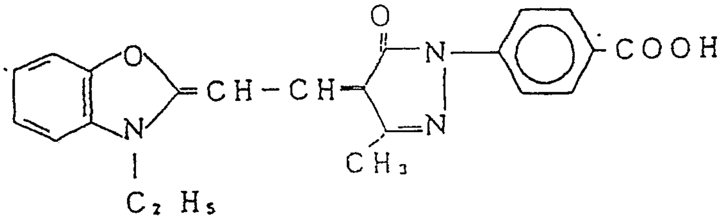

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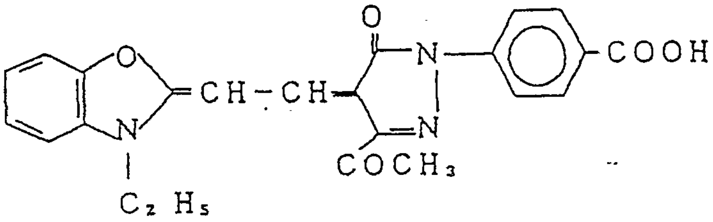

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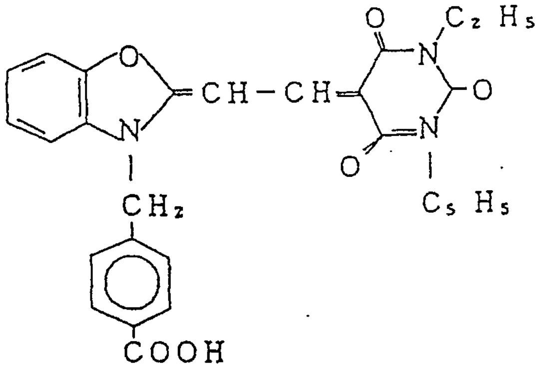

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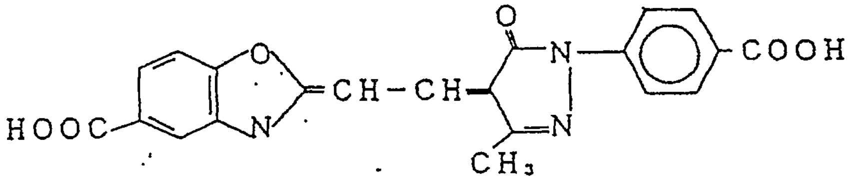

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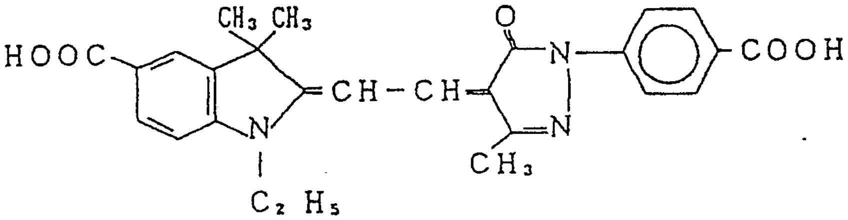

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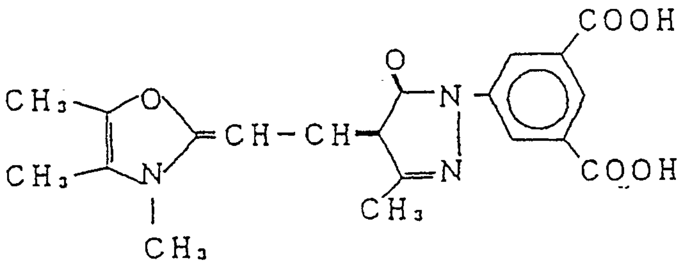

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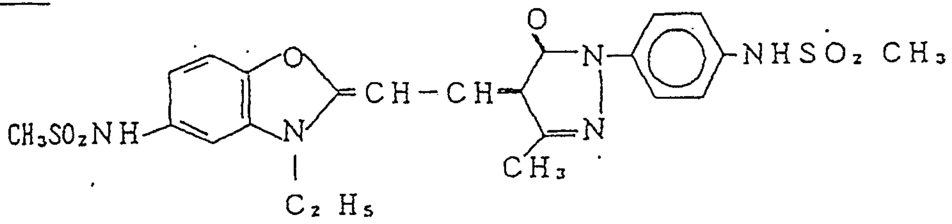

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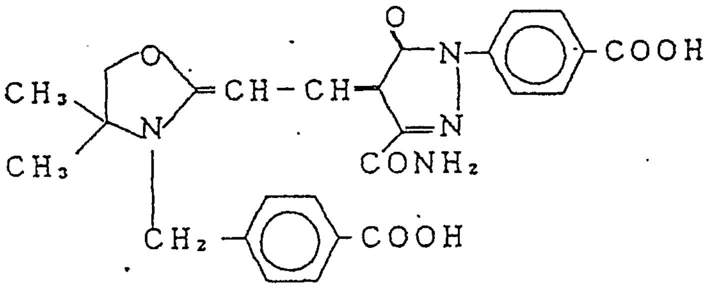

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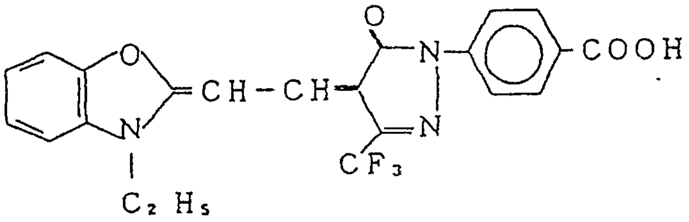

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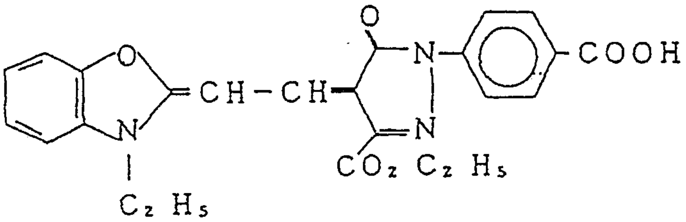

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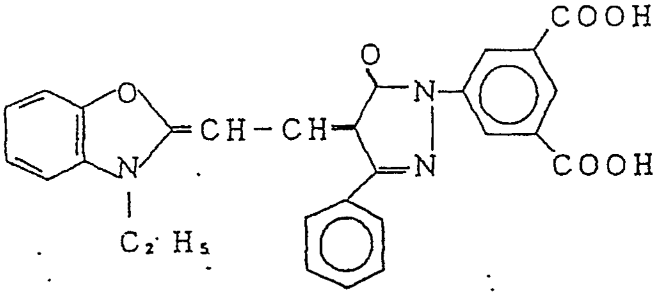

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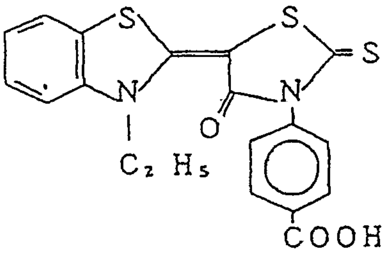

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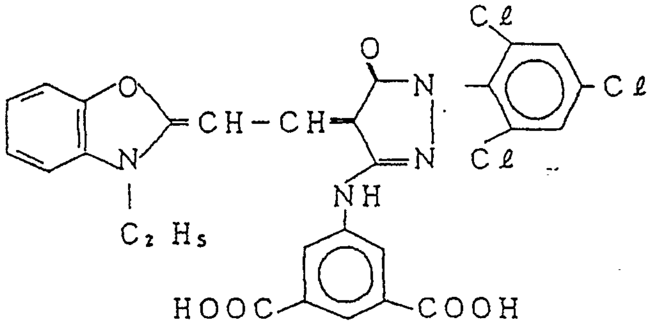

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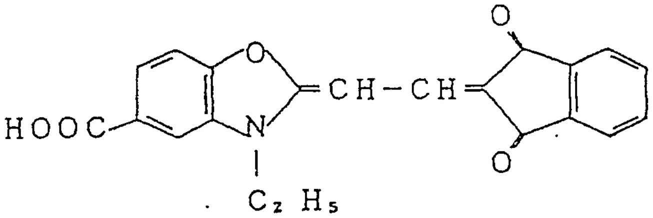

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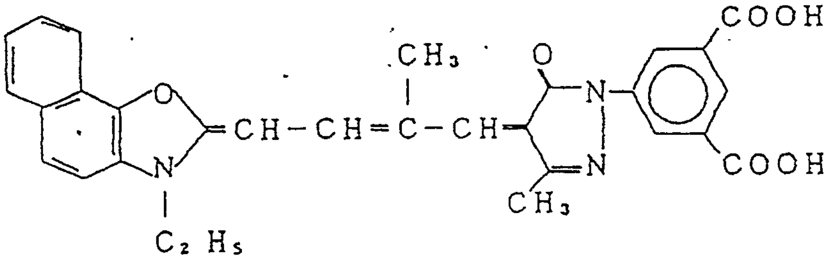

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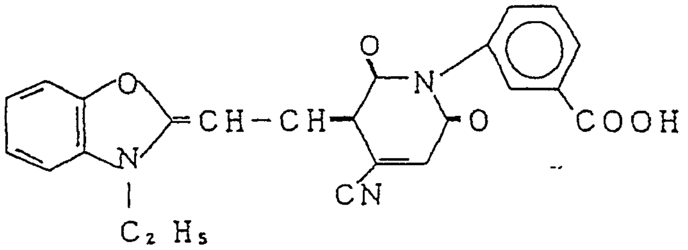

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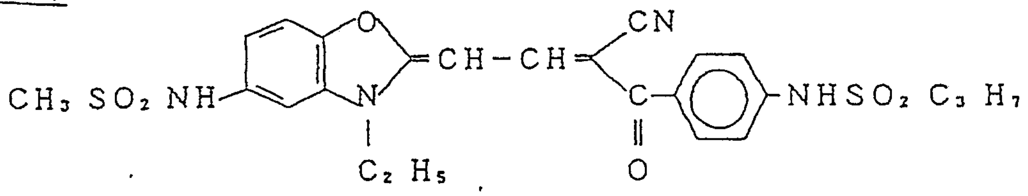

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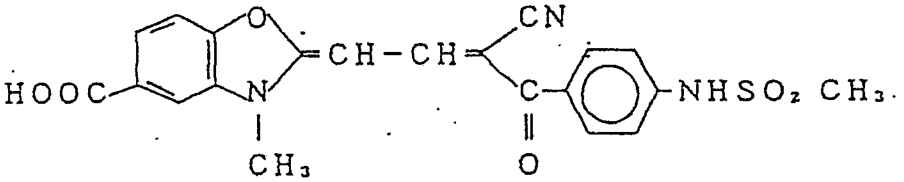

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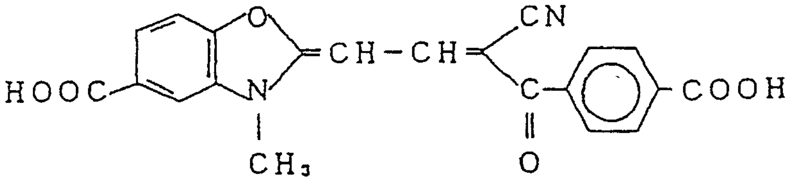

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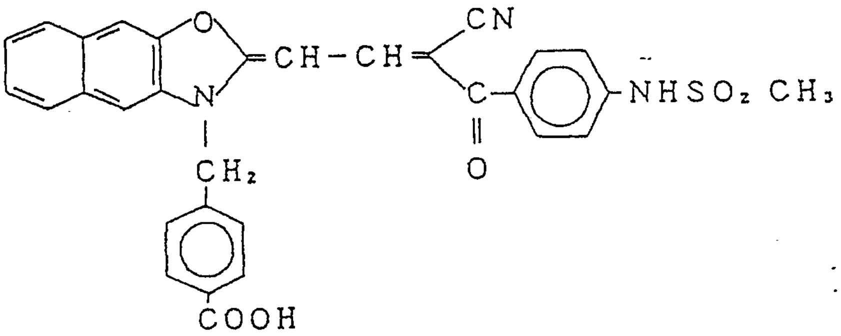

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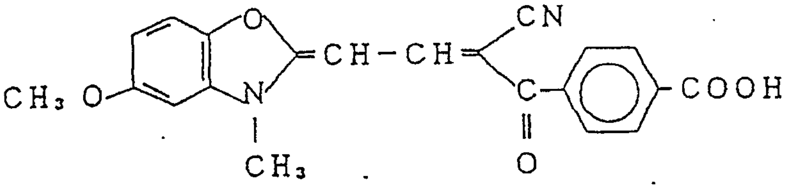

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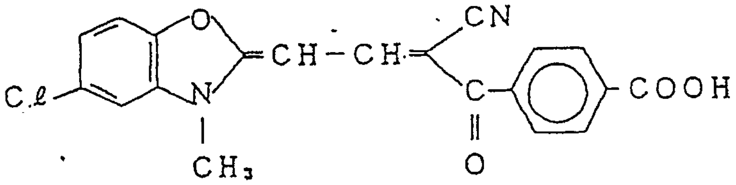

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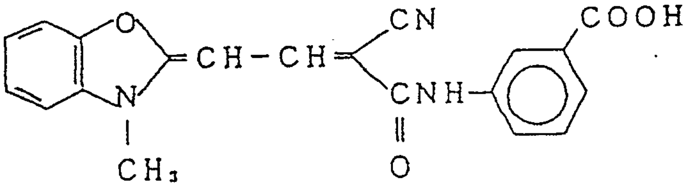

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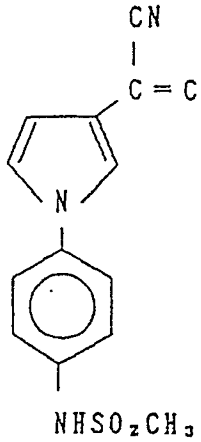

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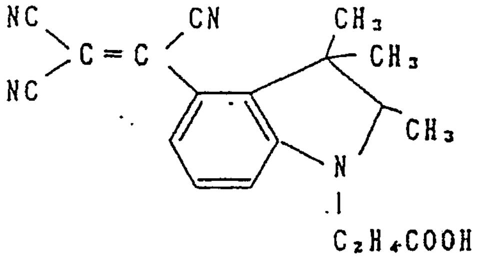

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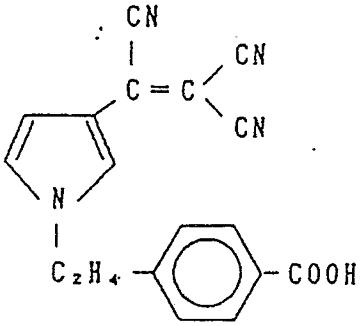

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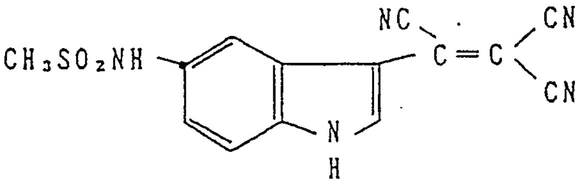
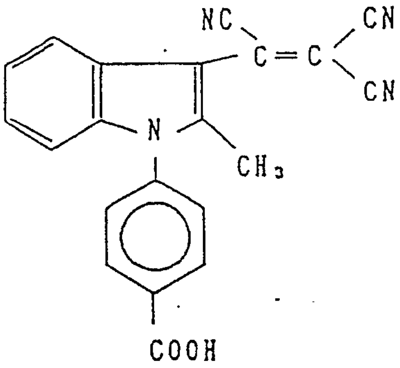
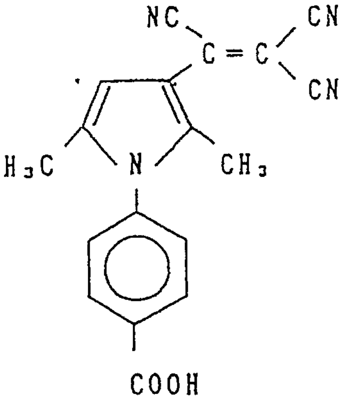

CH₃SO₂NH
NC
C=C
CN
CN
N
H

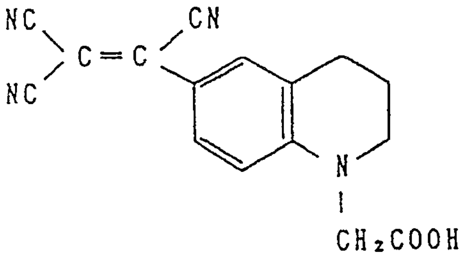
(VI-5)


NC
C=C
CN
CN
N
CH₃
COOH

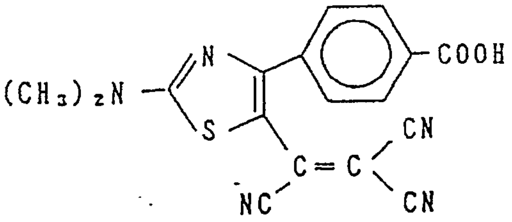
(VI-6)


NC
C=C
CN
CN
H₃C
N
CH₃
COOH

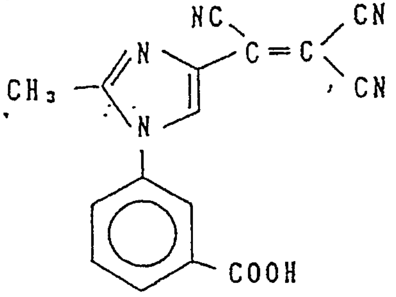
(VI-7)


NC
CN
NC
C = C
N
CH₂COOH

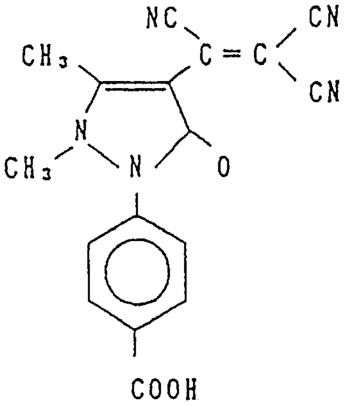
(VI-8)


(CH₃)₂N
N
S
COOH
CN
C = C
NC
CN

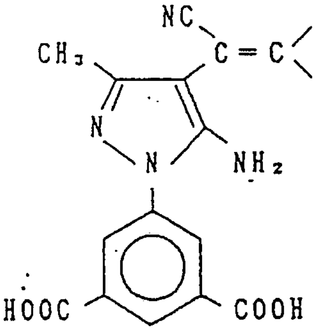
(VI-9)


NC
CN
C = C
CN
N
CH₃
N
COOH

(VI-10)



(VI-11)



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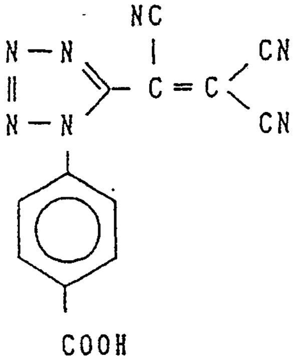
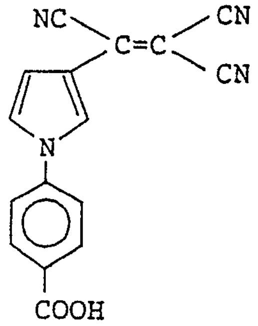


(VI-13)



The dyes for use in the present invention are readily prepared using the methods disclosed, for example, in World Patent WO 88/04794, European Patents EP 0274723A1, 276,566 and 299,435, JP-A-52-92716, JP-A-55-155350, JP-A-55-155351, JP-A-61-205934, JP-A-48-68623, and U.S. Patents 2,527,583, 3,486,897, 3,746,539, 3,933,798, 4,130,429 and 4,040,841, and using other methods based upon these methods.

The above described dyes are formed into a solid fine powder dispersion for incorporation into a hydrophilic layer which are established in the photographic material of the present invention. The fine powder dispersion can be formed by suspending the dye in the form of a dispersion, and/or using a known method of forming fine particles, such as ball milling (using a ball mill, vibrating ball mill or a planetary ball mill for example), sand milling, colloid milling, jet milling or roller milling for example, in the presence of a dispersing agent. A solvent, for example water or alcohol may also be present in preparing the dispersion. Alternatively, the dye may be dissolved in a suitable solvent and then fine crystals of the dye may be precipitated by adding a poor solvent for the dye, wherein surfactants can be added for dispersion. Alternatively, the dye can be crystallized using pH control by first dissolving the dye and then adjusting the pH. The dye particles in the dispersion are such that the average particle diameter is not more than 10 μm, preferably not more than 2 μm, and most desirably not more than 0.5 μm and, depending on the particular appication, fine powders of particle size not more than 0.1 μm are especially desirable. Other method to form a solid fine powder dispersion of dyes is described, for example, in WO 88/04794.

The amount of dye incorporated into a hydrophilic colloid layer of the photographic material of the present invention is within the range from 1 to 1000 mg/m^2, and preferably within the range from 5 to 800 mg/m^2.

The dye dispersion of the present invention can be added to any hydrophilic colloid layer including emulsion layers and intermediate layers.

The effect of the present invention is especially pronounced when the dye is used to replace part or all of the colloidal silver which is generally used in a yellow filter layer and/or anti-halation layer.

Compounds of formula (VII) for use in the present invention are described below.

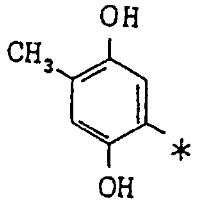
The group A in formula (VII) is described in detail. The redox nucleus represented by A is, for example, a hydroquinone, a catechol, a p-aminophenol, an o-aminophenol, a 1,2-naphthalenediol, a 1,4-naphthalenediol, a 1,6-naphthalenediol, a 1,2-aminonaphthol, a 1,4-aminonaphthol or a 1,6-aminonaphthol nucleus. The amino group is preferably substituted with a sulfonyl group having from 1 to 25 carbon atoms or an acyl group having from 1 to 25 carbon atoms. The sulfonyl group may be a substituted or unsubstituted aliphatic sulfonyl group or aromatic sulfonyl group. Furthermore, the acyl group may be a substituted or unsubstituted aliphatic acyl group or aromatic acyl group. The hydroxyl group or amino group which forms the redox nucleus of A may be protected with a protecting group which is removeable during development processing. Examples of protecting groups include those having from 1 to 25 carbon atoms and include acyl groups, alkoxycarbonyl groups, carbamoyl groups and the groups disclosed, for example, in JP-A-59-197037 and JP-A-59-201057. Moreover, these protecting groups may be joined to the substituent groups of A described below when the substituent group are protecting group join to form a five, six or seven membered ring.

The redox nucleus represented by A may have substituent groups. Examples of useful substituent groups are those having not more than 25 carbon atoms, and include alkyl groups, aryl groups, alkylthio groups, arylthio groups, alkoxy groups, aryloxy groups, amino groups, amido groups, sulfonamido groups, alkoxycarbonylamino groups, ureido groups, carbamoyl groups, alkoxycarbonyl groups, sulfamoyl groups, sulfonyl groups, cyano groups, halogen atoms, acyl groups, carboxyl groups, sulfo groups, nitro groups, heterocyclic residues and -(Time)$_t$-X groups for example. These substituent groups may be further substituted with the substituent groups described above. Furthermore, the substituent groups can join together where possible to form a saturated or an unsaturated carbocyclic ring or a saturated or unsaturated heterocyclic ring.

Preferred examples of A include hydroquinone, catechol, p-aminophenol, o-aminophenol, 1,4-naphtha lenediol and 1,4-aminonaphthol. Particularly preferred examples of A are hydroquinone, catechol, p-amylphenol and o-aminophenol nuclei. Moreover, A is most desirably hydroquinone nucleus.

Useful examples of compounds represented by A in formula (VII) are indicated below. The asterisk in each structural formula indicates the position at which the -(Time)$_x$-Z group is bonded.

(1)



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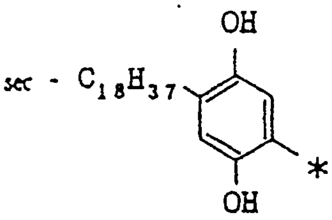

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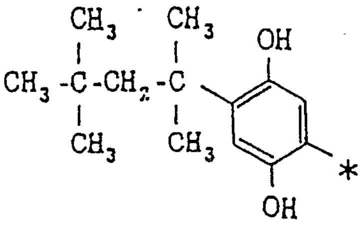
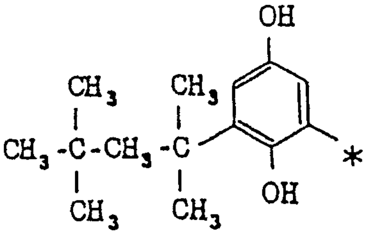
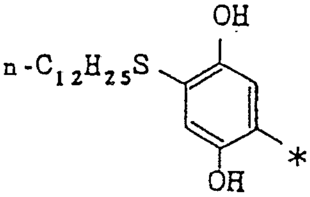

CH3
CH3
OH
CH3-C-CH2-C
CH3
CH3
OH
*

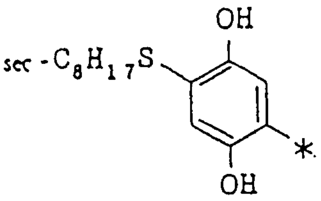
(4)


OH
CH3
CH3
CH3-C-CH3-C
CH3
CH3
OH
*

(5)


OH
n-C12H25S
OH
*

(6)



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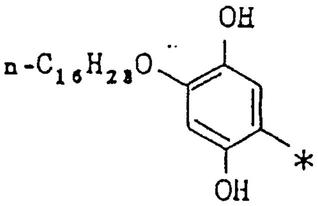

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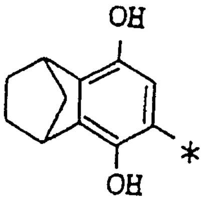

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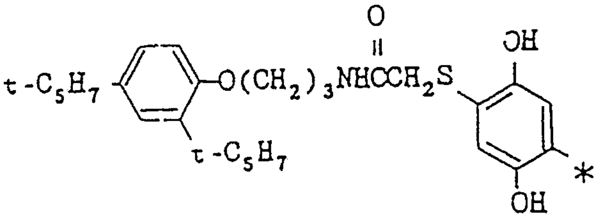

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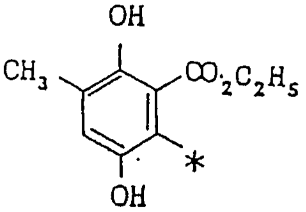

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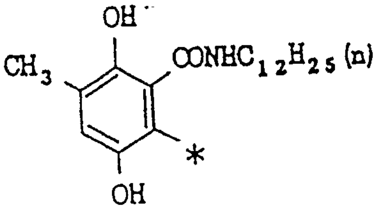

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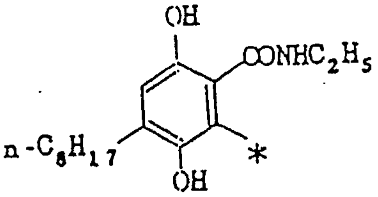

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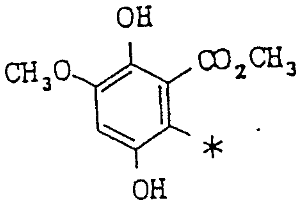
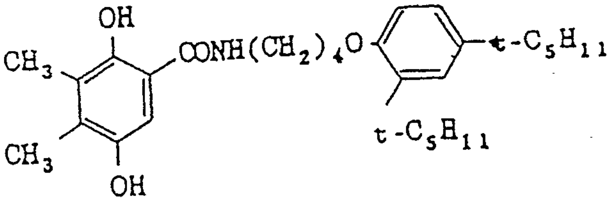
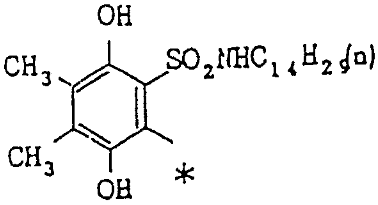

OH
CH3O
CO2CH3
*
OH

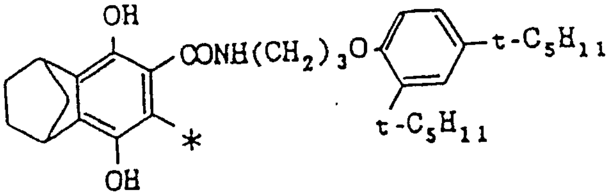
(14)


OH
CH3
CONH(CH2)4O
t-C5H11
CH3
t-C5H11
OH

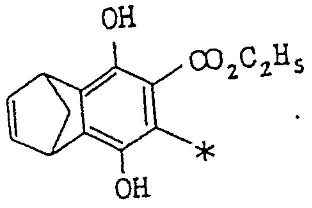
(15)


OH
CH3
SO2NHC14H29(n)
CH3
OH
*

(16)


OH
CONH(CH2)3O
t-C5H11
t-C5H11
*
OH

(17)



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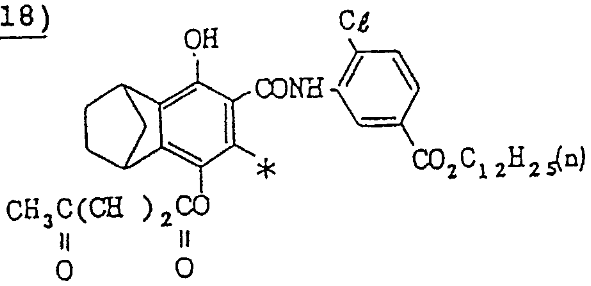

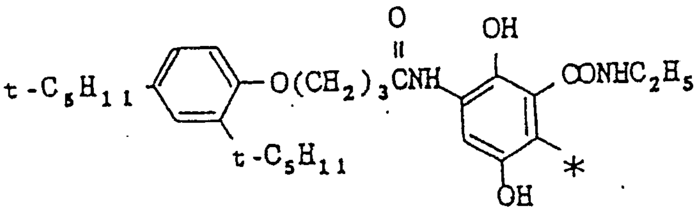

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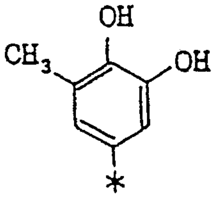

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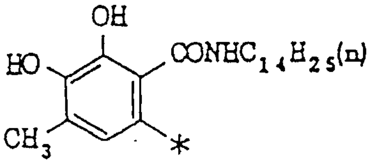

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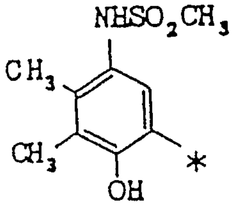

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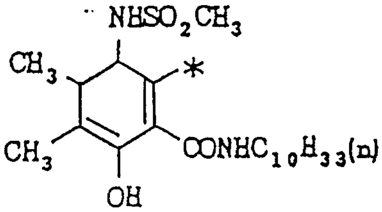

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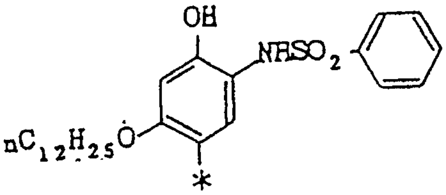

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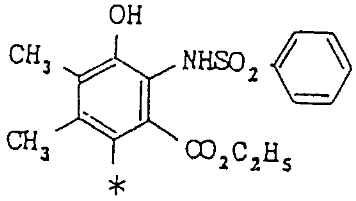
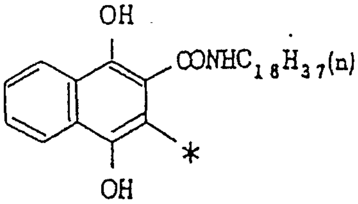
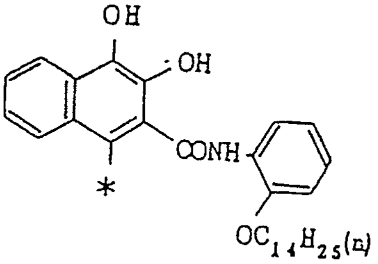

OH
CH3
CH3
NHSO2
CO2C2H5
*

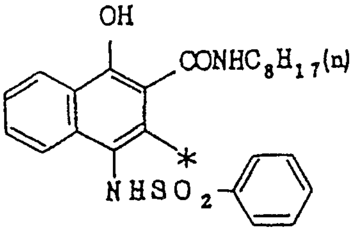
(26)


OH
CONHC18H37(n)
*
OH

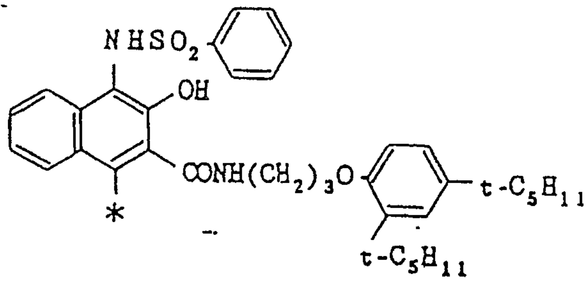
(27)


OH
OH
CONH
*
OC14H25(n)

(28)


OH
CONHC8H17(n)
*
NHSO2

(29)


NHSO2
OH
CONH(CH2)3O
t-C5H11
t-C5H11
*

The group -(Time)$_t$-Z of formula (VII) is a group which is released as $^{\ominus}$-(Time)$_t$-Z when the redox nucleus represented by A in formula (VII) undergoes a cross-oxidation reaction during development and assumes an oxidized form.

Time is a timing group with is linked to A via a sulfur atom, a nitrogen atom, an oxygen atom or a selenium atom, and which releases Z via a single stage reaction or a two or more stage reaction from the $^{\ominus}$-(Time)$_t$-Z group which is released during development. The groups disclosed, for example, in U.S. Patents 4,248,962 and 4,409,323, British Patent 2,096,783, U.S. Patent 4,146,396, JP-A-51-146828 and JP-A-57-56837 are examples of the Time group. The Time group may also be comprised of a combination of two or more groups selected from among those disclosed in the above cited doouments.

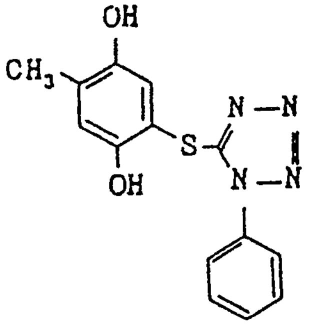
Z represents a development inhibitor. Examples of the development inhibitor include compounds which have a mercapto group bonded to a heterocyclic ring, and a heterocyclic compound which can form imino-silver. Examples of compounds which have a mercapto group bonded to a heterocyclic ring include substituted or unsubstituted mercaptoazoles (for example, 1-phenyl-5-mercaptotetrazole, 1-propyl-5-mercaptotetrazole, 1- butyl-5-mercaptotetrazole, 2-methylthio-5-mercapto-1,3,4-thiadiazole, 3-methyl-4-phenyl-5-mercapto-1,2,4-triazole, 1-(4-ethylcarbamoylphenyl)-2-mercaptoimidazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-phenyl-5-mercapto-1,3,4-oxadiazole, 1-{3-(3-methylureido)phenyl}-5-mercaptotetrazole, 1-(4-nitrophenyl)-5-mercaptotetrazole, 5-(2-ethylhexanoylamino)-2-mercaptobenzimidazole), substituted or unsubstituted mercaptoazaindenes (for example, 6-methyl-4-mercapto-1,3,3a,7-tetra-azaindene, 4,6-dimethyl-2-mercapto-1,3,3a,7-tetraazaindene), and substituted or unsubstituted mercaptopyrimidines (for example, 2-mercaptopyrimidine, 2-mercapto-4-methyl-6-hydroxypyrimidine).

Examples of the heterocyclic compound which can form imino-silver include substituted and unsubstituted triazoles (for example, 1,2,4-triazole, benzotriazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-bromobenzotriazole, 5-n-butylbenzotriazole, 5,6-dimethylbenzotriazole), substituted or unsubstituted indazoles (for example, indazole, 5-nitroindazole, 3-nitoindazole, 3-chloro-5-nitroindazole) and substituted or unsubstituted benzimidazoles (for example, 5-nitrobenzimidazole, 5,6-dichlorobenzimidazole).

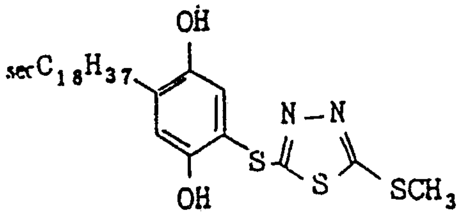
Furthermore, Z may be a species which is eliminated from Time in general formula (VII) and which, after forming a compound which has development inhibiting properties, undergoes a chemical reaction with the components of the development bath to be converted into a compound which has substantially no development inhibiting effect or which has a markedly reduced development inhibiting effect. Functional groups which undergo chemical reactions of this type include ester groups, carbonyl groups, imino groups, immonium groups, Michael addition acceptor groups and imide groups. Examples of such deactivatable development inhibitors include 1-(3-phenoxycarbonylphenyl)-5-mercaptotetrazole, 1-(4-phenoxycarbonylphenyl)-5-mercaptotetrazole, 1-(3-maleinimidophenyl)-5-mercaptotetrazole, 5-phenoxycarbonylbenzotriazole, 5-(4-cyanophenoxycarbonyl)benzotriazole, 2-phenoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole, 5-nitro-3-phenoxycarbonylimidazole, 5-(2,3-dichloropropyloxycarbonyl)benzotriazole, 1-(4-benzoyloxyphenyl)-5-mercaptotetrazole, 5-(2-methanesulfonylethoxycarbonyl)-2-mercaptobenzothiazole, 5-cinnamoylaminobenzotriazole, 1-(3-vinylcarbonylphenyl)-5-mercaptotetrazole, 5-succinimidomethylbenzotriazole, 2-{4-succinimidophenyl}-5- mercapto-1,3,4-oxadiazole and 6-phenoxycarbonyl-2-mercaptobenzoxazole.

Useful examples of compounds represented by formula (VII) are provided below, but the present invention is not to be construed as being limited to these examples.

(VII-1)



(VII-2)



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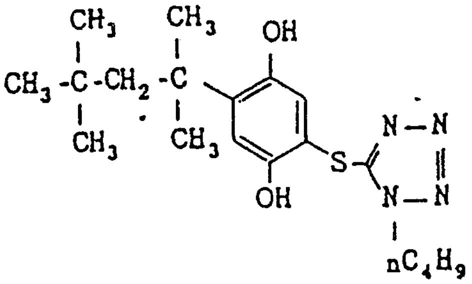
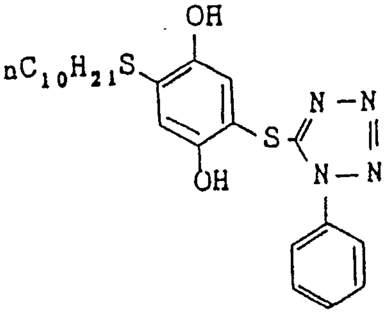
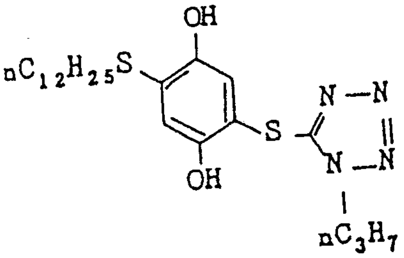


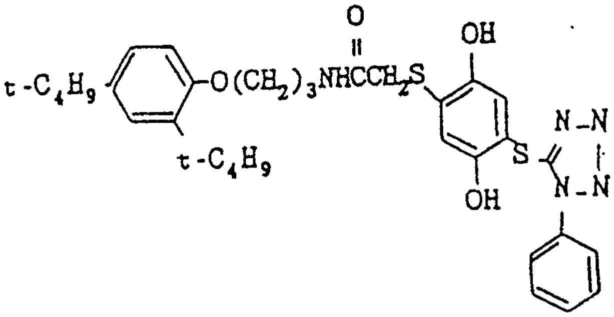
(VII-4)



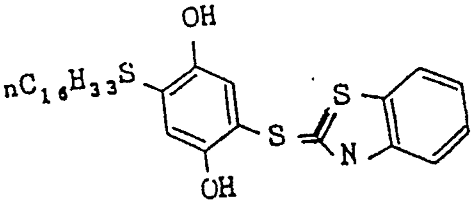
(VII-5)



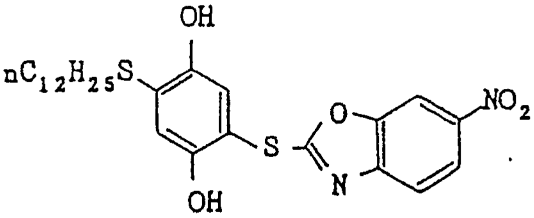
(VII-6)



(VII-7)



(VII-8)



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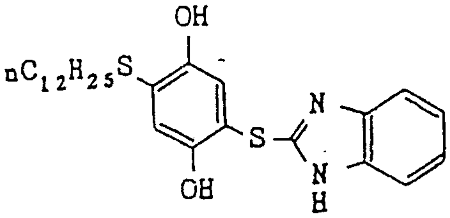

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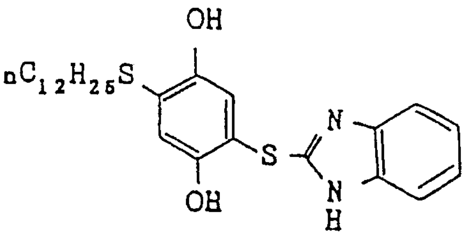

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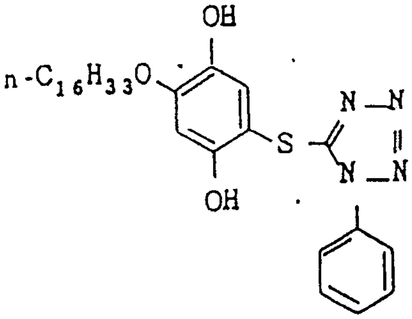

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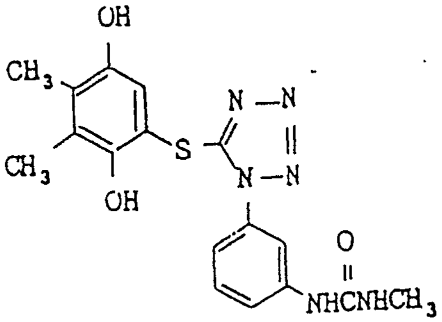

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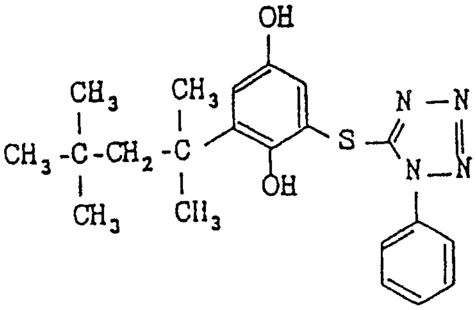

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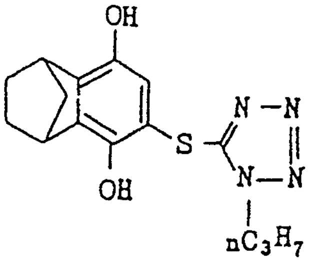

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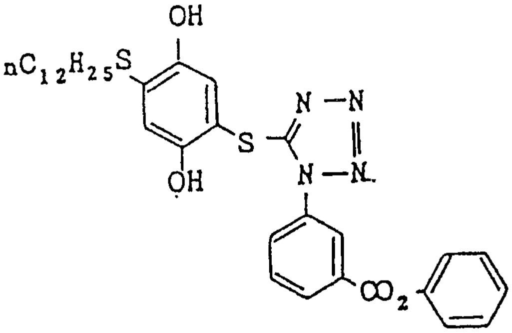

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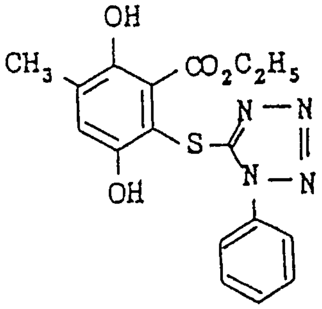

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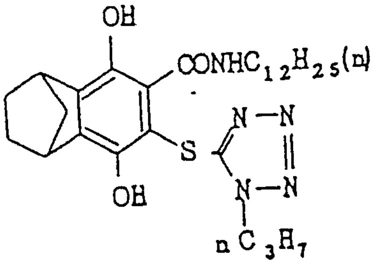

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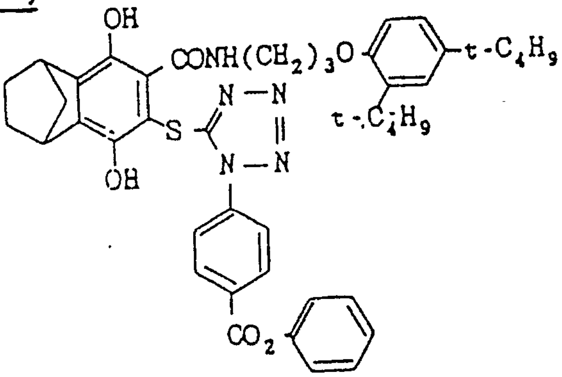

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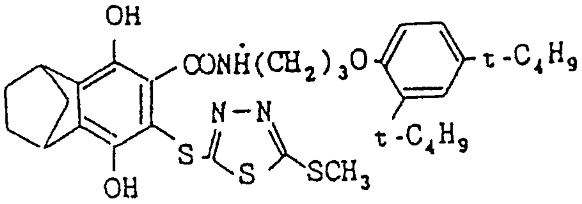

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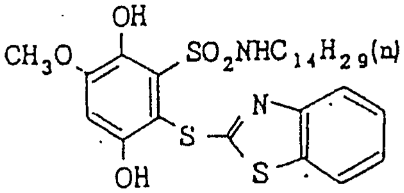

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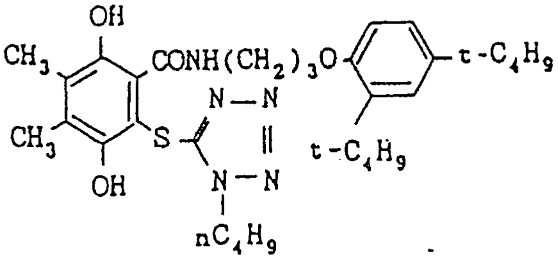

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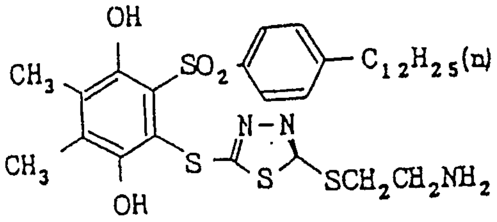

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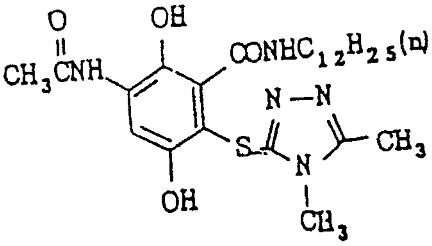

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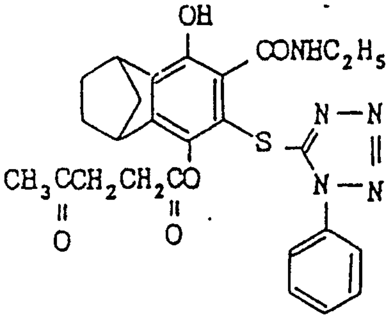

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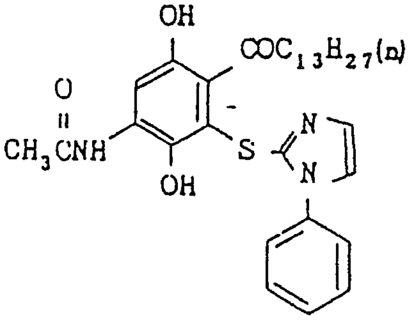

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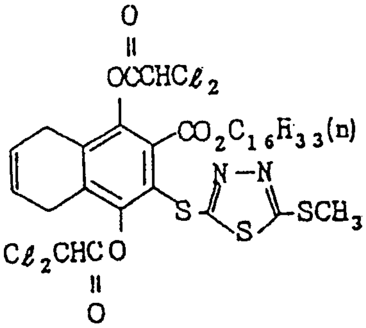

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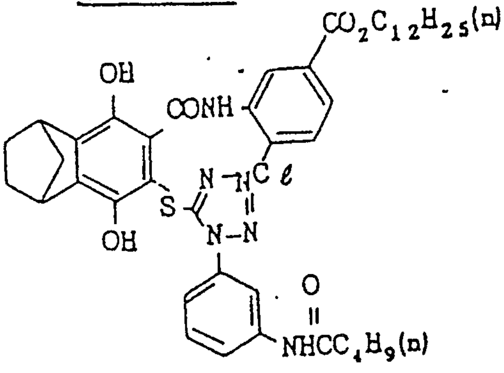

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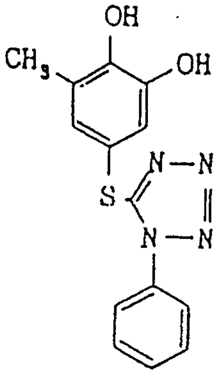

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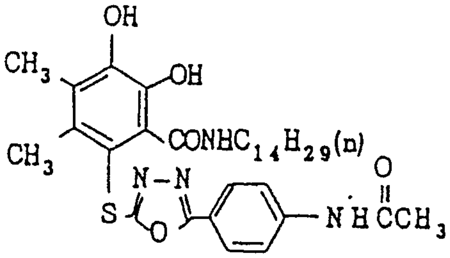

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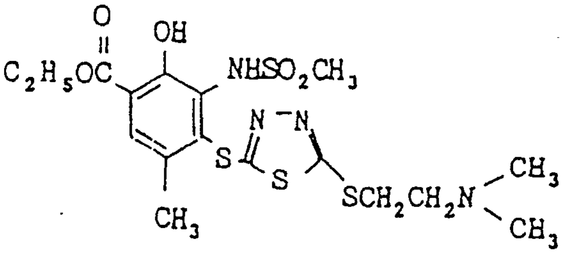

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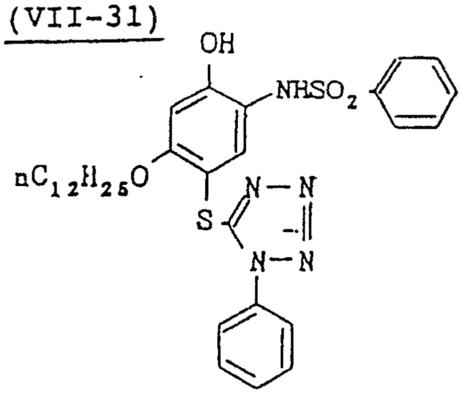

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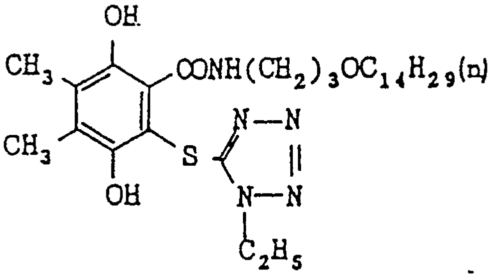

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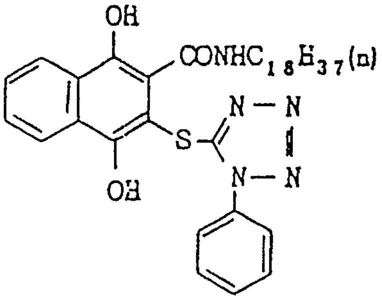

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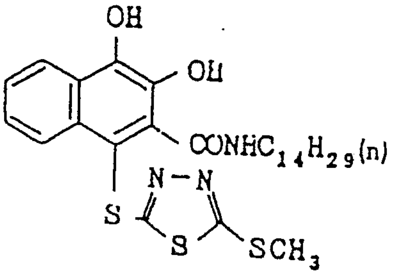

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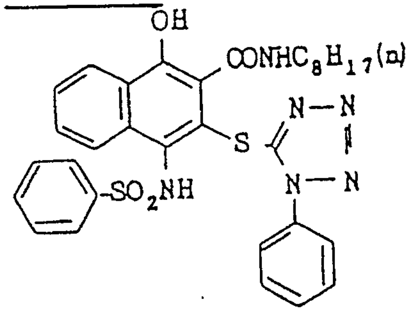

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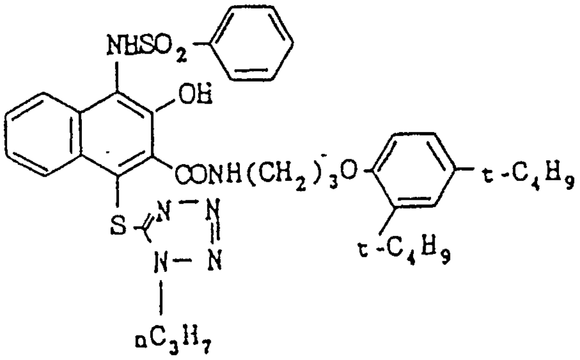

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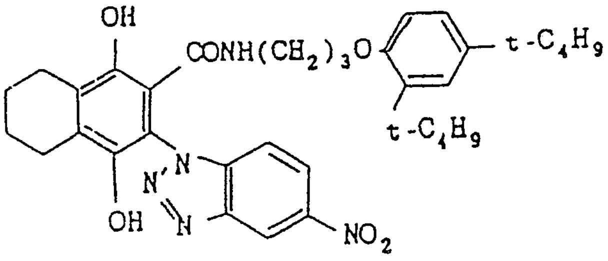

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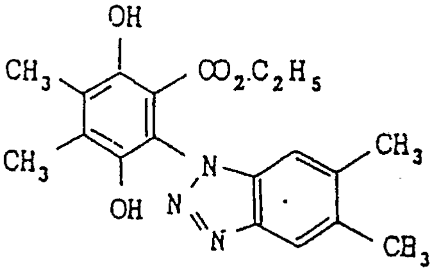

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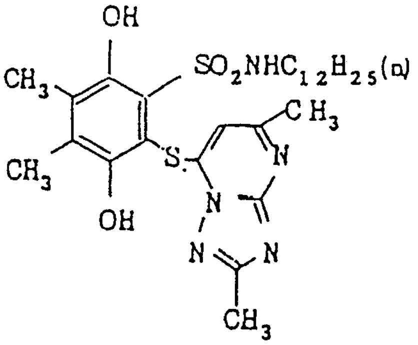

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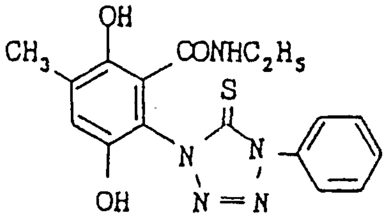

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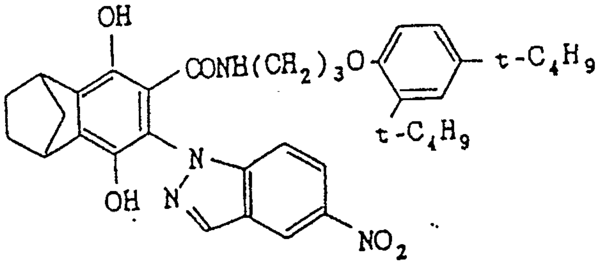

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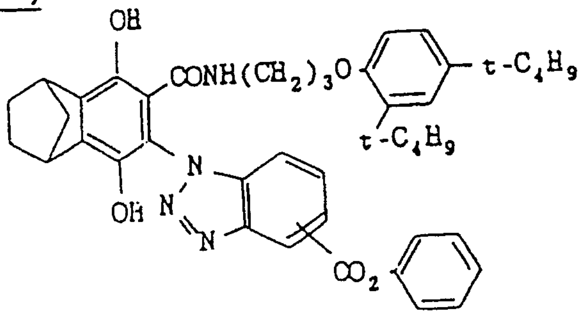

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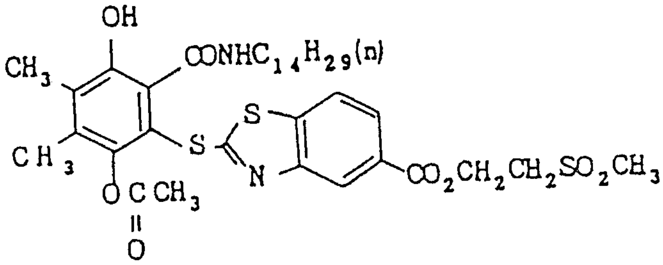

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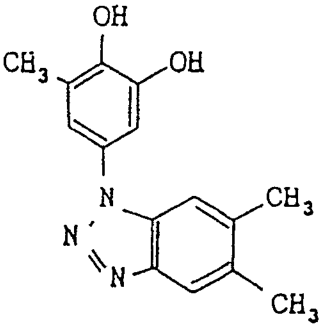

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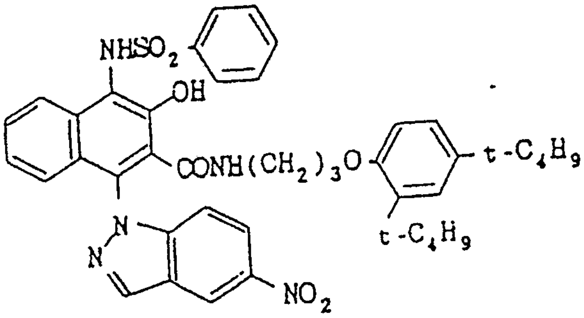

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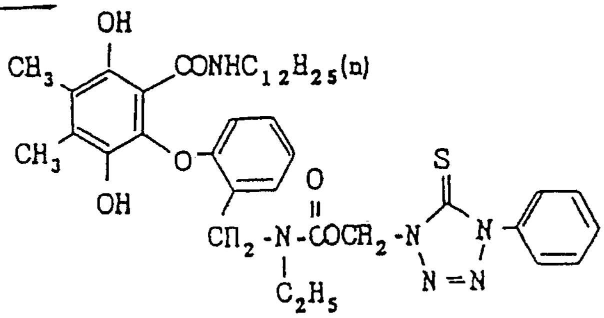

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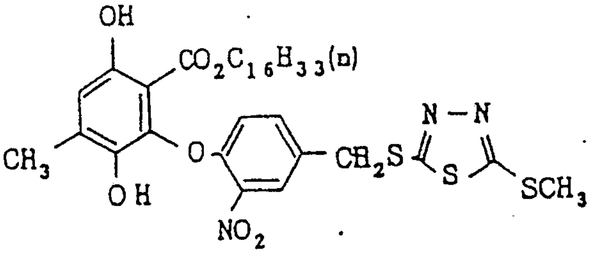

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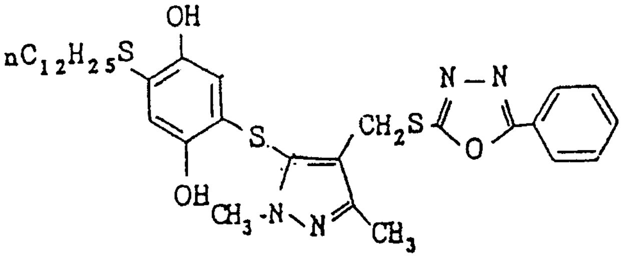

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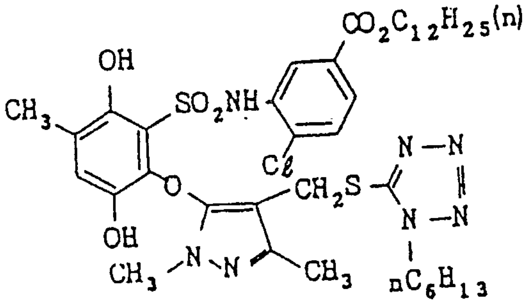

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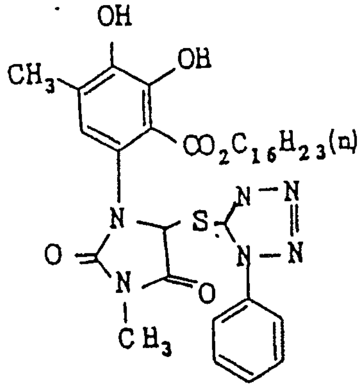

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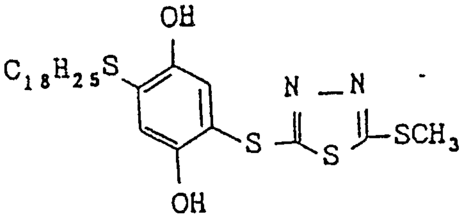


Compounds represented by formula (VII) can generally be prepared using one of the two methods described below. Firstly, when Time represents a bond (t = 0), a development inhibitor is reacted at a temperature ranging from room temperature to 100 °C with a benzoquinone, orthoquinone, quinone monoimine or quinone di-imine derivative in chloroform, 1,2-dichlorethane, carbon tetrachloride or tetrahydrofuran in the absence of a catalyst or in the presence of a catalyst such as p-toluenesulfonic acid, benzenesulfonic acid, trifluoromethanesulfonic acid or methanesulfonic acid, for example. In a second method, a development inhibitor is reacted at a temperature between -20 °C and 100 °C with a benzoquinone, orthoquinone, quinone monoimine or quinone di-imine derivative which has been substituted with chlorine, bromine or iodine in the presence of a base such as potassium carbonate, sodium bicarbonate, sodium hydride or triethylamine, for example, in an aprotic polar solvent such as acetone, tetrahydrofuran or dimethylformamide, for example, and the quinone thus obtained is reduced with a reducing agent such as diethylhydroxylamine or sodium hydrosulfite for example. Literature References which may be consulted include Research Disclosure 18227 (1979) and Liebigs Ann, Chem. , 764.131 (1972).

Synthesis is also achieved using similar methods as those described above in cases where the release of Z occurs via a Time group. Namely, methods can be used in which Time-Z is used instead of the development inhibitor (Z) as described above or methods in which Time which has a group which can be substituted by Z (for example, a halogen atom, a hydroxyl group or a precursor thereof) is first introduced into the redox nucleus and then Z is bound by a substitution.

The addition amount of the compound represented by formula (VII) of the present invention is within the range of from 10^{-5} to 10^{-1} mol, and preferably within the range of from 10^{-4} to 10^{-2} mol, per mol of silver halide in the layer to which the compound is added. When the compound represented by formula (VII) is incorporated into a hydrophilic colloidal layer containing no silver halide, the addition amount of the compound is within the range of from 10^{-7} to 10^{-3} mol per m^2 of the colloidal layer and more preferably 10^{-6} to 10^{-4} mol per m^2 of the colloidal layer.

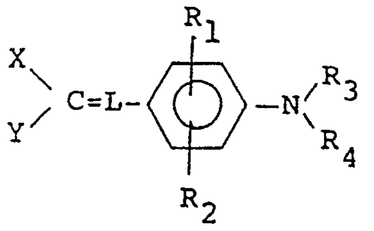
The compound represented by formula (VII) of the present invention can be used alone, or incombination of two or more thereof.

The compound represented by formula (VII) can be added as an emulsion which has been obtained by dissolution and high speed agitation in a high boiling point oil, or by dissolving the compound in a water soluble organic solvent such as alcohol or cellosolve, for example, and adding the emulsion thus obtained with agitation to an aqueous gelatin solution to achieve dispersion.

The compound represented by formula (VII) of the present invention is used in a hydrophilic colloidal layer containing silver halide or containing no silver halide such as a yellow filter layer, antihalation layer, an intermediated layer and a protective layer.

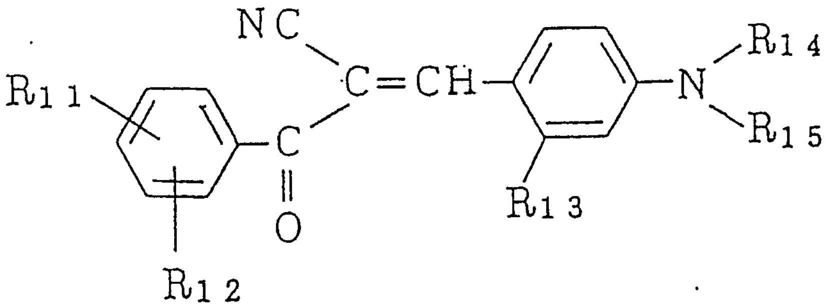
The compound selected from the group represented by formulae (I) to (VI) and the compound represented by formula (VII) may be incorporated into the same layer or different layers.

It is preferred to use a dye represented by following formula (A) for the yellow filter layer:



(A)

wherein X and Y, which may be the same or different, each represents a cyano group, a carboxy group, an alkylcarbonyl group, an arylcarbonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a sulfonyl group, or a sulfamoyl group, said X and Y may combine with each other to form a ring; R_1 and R_2, which may be the same or different, each represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxy group, a carboxy group, a substituted amino group, a carbamoyl group, a sulfamoyl group, or an alkoxycarbonyl group; R_3 and R_4, which may be the same or differet, each represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an acyl group, or a sulfonyl group, and a 5- or 6-membered ring may be formed by R_3 and R_4; also, said R_1 and R_3 or R_2 and R_4 may combine with each other to form a 5-or 6-membered ring; and L represents a methine group. Preferred compounds in the compounds shown by the formula (A) are shown by following formula (AI)



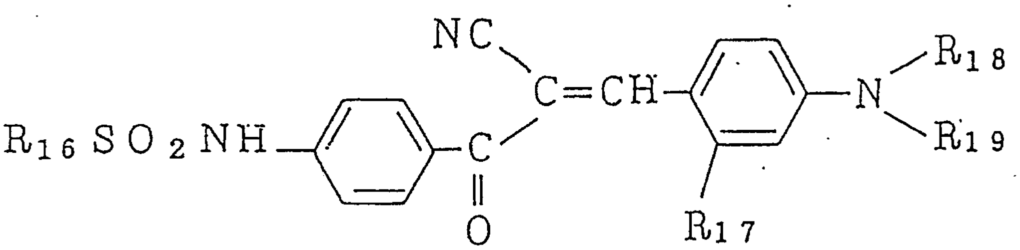
(AI)

wherein R_{11} represents a hydrogen atom or an electron donative group, and preferably represents an electron donative group having a Hammett's σp value of not larger than -0.05, such as, for example, an alkyl group, a cycloalkyl group, a hydroxy group, an alkoxy group, an amino group, and a ureido group.

The aforesaid Hammett's σp value can be selected based on the table described in Yakubutsu no Kozo Kassei Sokan (Co-Relation of Structural Activities of Medicaments) , pages 96-103(1979), published by Nanko Do.

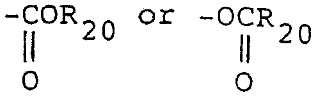
In the formula, R_{12} represents a hydroxy group, RSO_2NH-, RCONH-, or RNHCONH- (wherein R represents a hydrocarbon group having from 1 to 6 carbon atoms); R_{13} represents a hydrogen atom, a halogen atom, a hydroxy group, an alkyl group having from 1 to 3 carbon atoms, an alkoxy group having from 1 to 3 carbon atoms, an alkylsulfonamido group having from 1 to 3 carbon atoms. or an alkylcarbonamido group having from 1 to 3 carbon atoms; and R_{14} and R_{15}, which may be the same or different, each represents an alkyl group having from 1 to 7 carbon atoms or a phenyl group.

In the compounds of shown by formula (AI), more preferred compounds are shown by following formula (AII):



(AII)

wherein R_{16} represents an alkyl group having from 1 to 3 carbon atoms; R_{17} represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms; R_{18} and R_{19}, which may be the same or the different, each represents an alkyl group having from 1 to 3 carbon atom, at least one of said R_{18} and R_{19} has

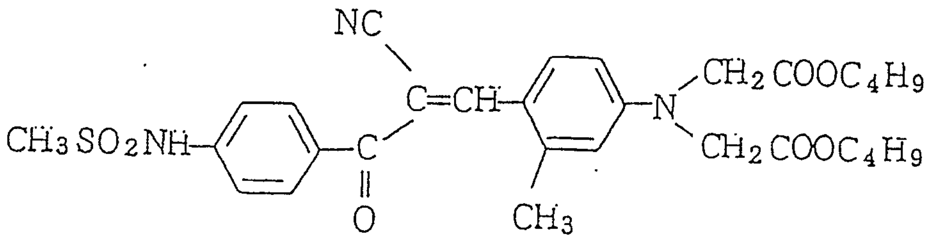


$$-\underset{\displaystyle O}{\underset{\|}{C}}OR_{20} \quad \text{or} \quad -O\underset{\displaystyle O}{\underset{\|}{C}}R_{20}$$

(wherein R_{20} represents an alkyl group having from 1 to 5 carbon atoms. which may be substituted.

Then, specific examples of the compounds used in this invention are illustrated below bue the invention is not limited thereto.

1.



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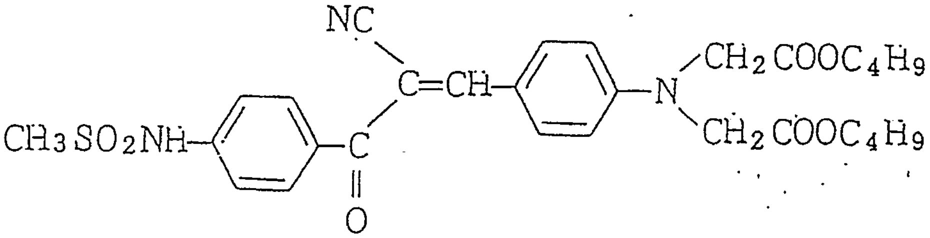

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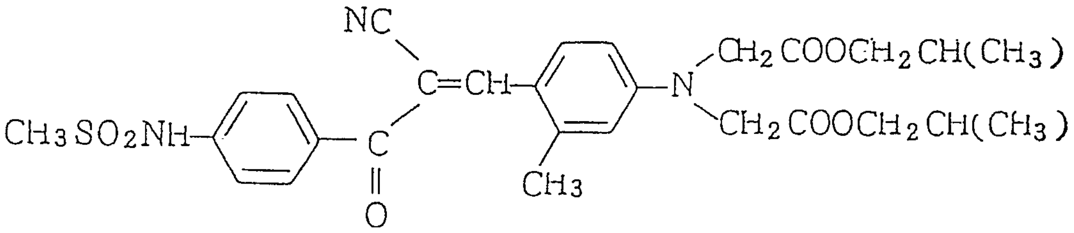

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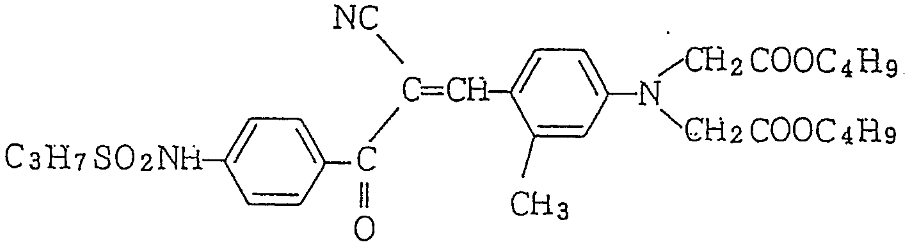

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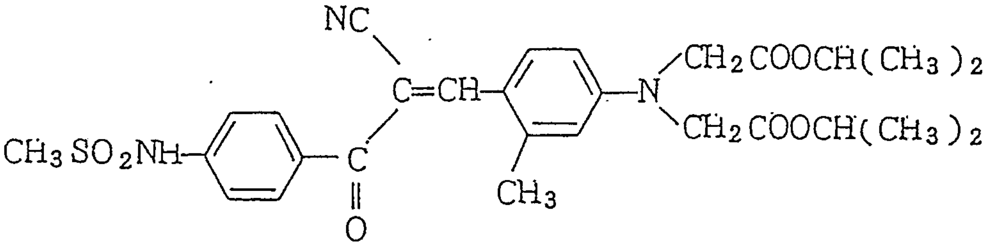

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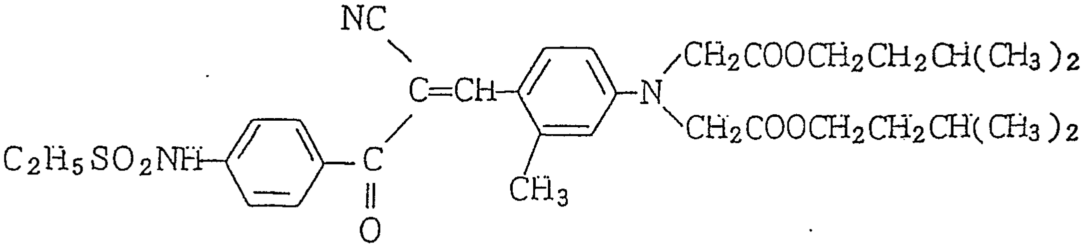

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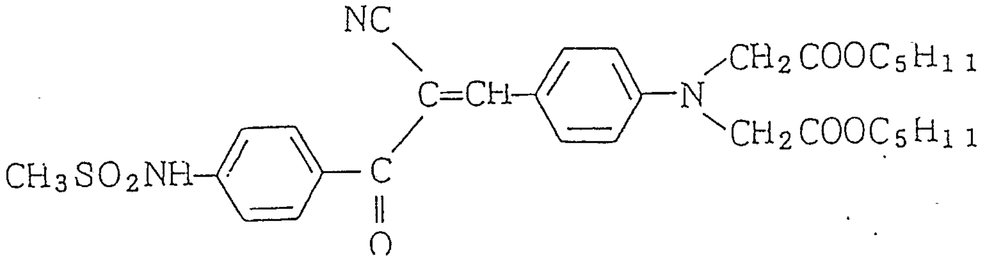

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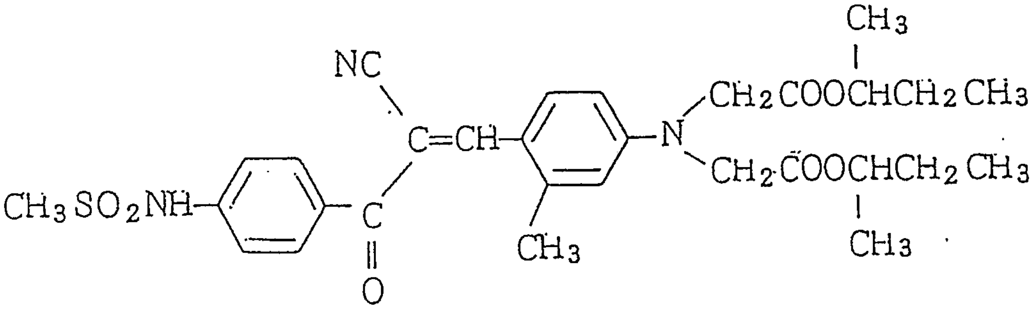

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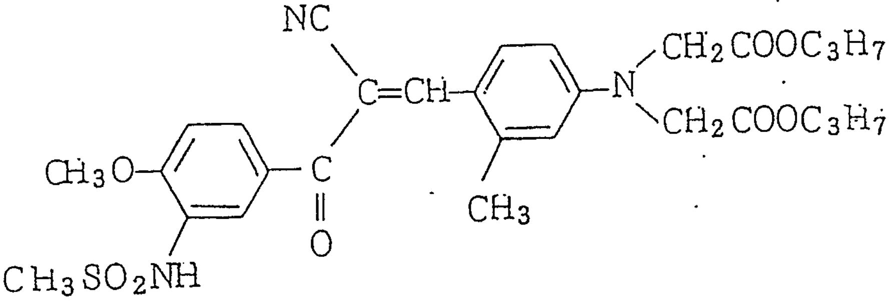

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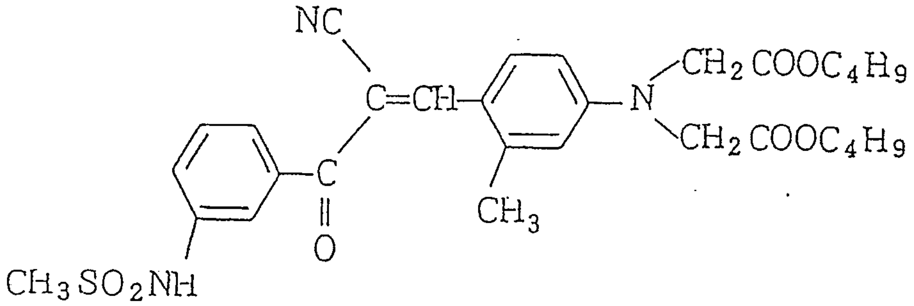
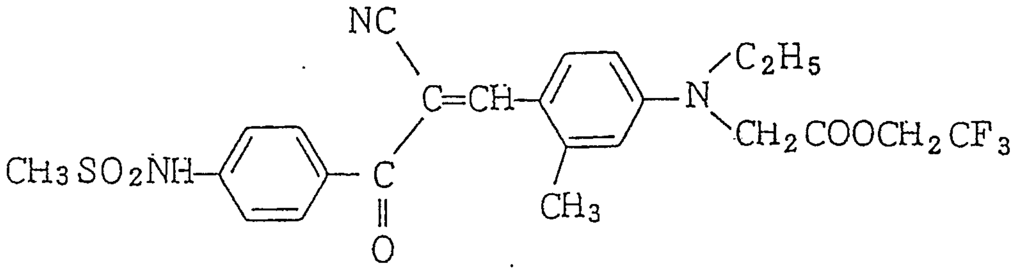


11.



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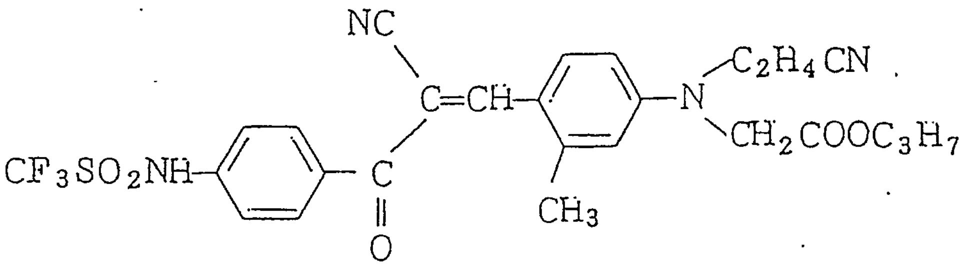

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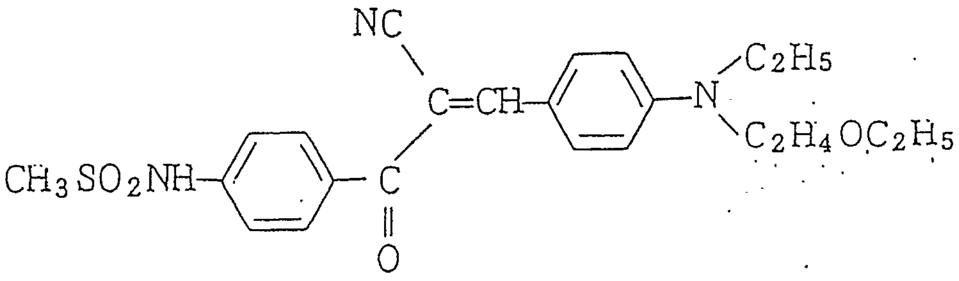

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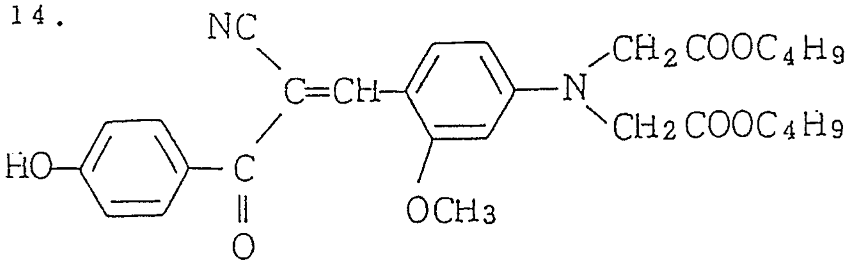

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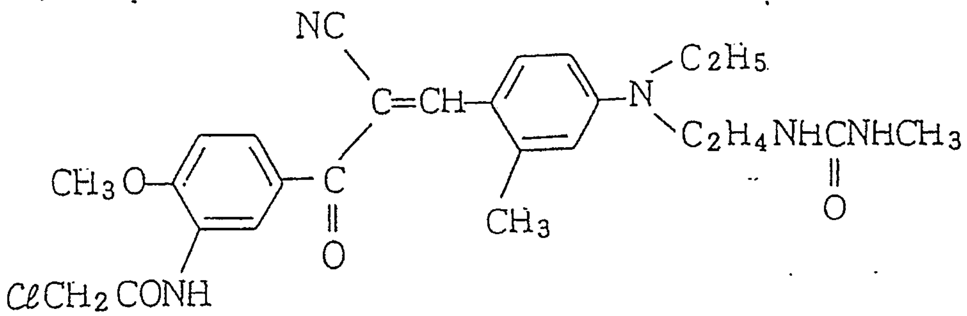

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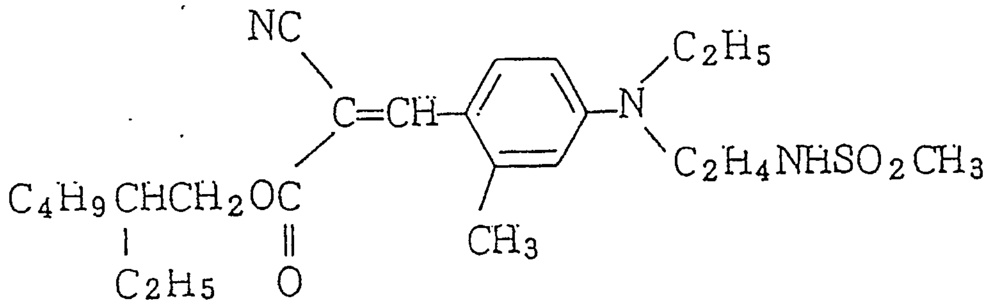

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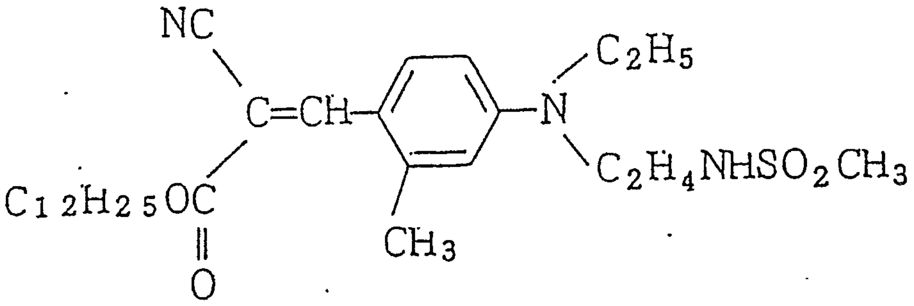

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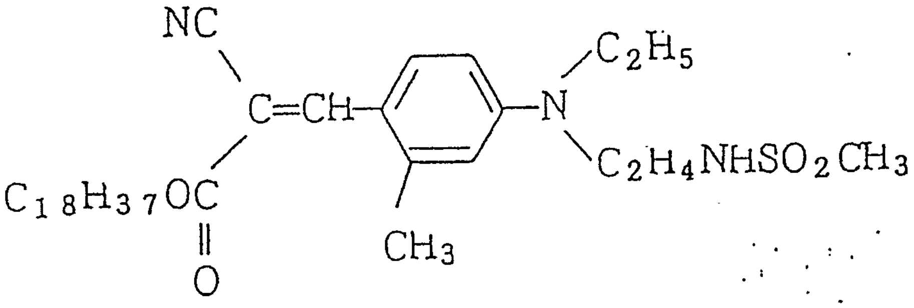


The dye compounds shown by formula (A) can be easily synthesized by the methods described in U.S. Patent 4,420,555, JP-A-62-222248, and JP-A-64-40827.

In general, the dye of formula (A) is used in an amount of from about 1 to 800 mg, and preferably from about 1 to 400 mg per square meter of the light-sensitive material.

The photographic photosensitive material of the present invention comprises a support having thereon at least one blue-sensitive layer, at least one green-sensitive layer and at least one red sensitive layer, but no particular limitation is imposed upon the number or order of the silver halide emulsion and other non-photosensitive hydrophilic colloid layers. Generally, the silver halide photographic material comprises at least one photosensitive layer comprising a plurality of silver halide layers which have substantially the same color sensitivity but different photographic speeds. The subject multilayer photosensitive layer is a unit photosensitive layer which is color sensitive to blue light, green light or red light, and the arrangement of the unit photosensitive layers within the photographic material generally involves the establishment of the layers in the order, from the support side, of a red-sensitive unit layer, green-sensitive unit layer, blue-sensitive unit layer. However, this order may also be reversed, as required, and the layers may be arranged such that a layer having a different color sensitivity is disposed between layers having the same color sensitivity.

Various non-photosensitive layers, such as intermediate layers, may be established between the silver halide photosensitive layers. Other non-photosensitive layers may also be provided as an uppermost layer and/or a lowermost layer.

The above noted intermediate layers may contain couplers and DIR compounds such as those disclosed in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037 and JP-A-61-20038, and may also contain generally used anti-color mixing compounds.

The plurality of silver halide emulsion layers constituting each unit photosensitive layer is preferably a double layer structure comprised of a high speed emulsion layer and a low speed emulsion layer as disclosed in West German Patent 1,121,470 or British Patent 923,045. Generally, arrangements in which the photographic speed is lower in the layer closer to the support are preferred, and non-photosensitive layers may be established between each of the silver halide emulsion layers. Furthermore, the low speed layers may be arranged on the side furthest away from the support and the high speed layers may be arranged on the side closest to the support as disclosed, for example, in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541 and JP-A-62-206543.

In practical terms, the arrangement may be, from the side furthest from the support, low speed blue sensitive layer(BL)/ high speed blue sensitive layer(BH)/ high speed green sensitive layer(GH)/ low speed green sensitive layer(GL)/ high speed red sensitive layer(RH)/ low speed red sensitive layer(RL), or BH/BL/GL/GH/RH/RL, or BH/BL/GH/GL/RL/RH.

Furthermore, the layers can be arranged in order, from the side furthest from the support, of blue sensitive layer/GH/RH/GL/RL as disclosed in JP-B-55-34932. (The term "JP-B" as used herein signifies an "examined Japanese patent publication".) Furthermore, the layers can also be arranged in order, from the side furthest away from the support, of blue sensitive layer/GL/RL/GH/RH, as disclosed in JP-A-56-25738 and JP-A-62-63936.

Furthermore, the unit layer comprising a high speed silver halide emulsion layer as an uppermost layer, an intermediate speed silver halide emulsion layer as an intermediate layer and a low speed silver halide emulsion layer as an undermost layer may be arranged so as to have different speeds with the lower speed layers disposed closer to the support, as disclosed in JP-B-49-15495. In the case of structures of this type having three layers of the same color sensitivity with different speeds, the layers in a unit layer of the same color sensitivity may be arranged in order, from the side furthest from the support, of intermediate speed emulsion layer/high speed emulsion layer/low speed emulsion layer, as disclosed in JP-A-59-202464.

Furthermore, the layers can be arranged in the order of high speed emulsion layer/low speed emulsion layer/intermediate speed emulsion layer, or low speed emulsion layer/intermediate speed emulsion layer/high sped emulsion layer, for example. The layers having four or more layers may be also modified in the order of layers as is described above.

As described above, various layer structures and arrangements can be selected according to the purpose of the photosensitive material.

The preferred silver halide for incorporation into the photographic emulsion layers of the photographic photosensitive material of this present invention include silver iodobromide, silver iodo chloride or silver iodochlorobromide containing not more than about 30 mol% of silver iodide. Most desirably, the silver halide is a silver iodobromide or silver iodochlorobromide containing from about 2 mol% to about 10 mol% of silver iodide.

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, a form which has crystal defects such as twinned crystal planes, or a form which is a composite of these forms.

The grain size of the silver halide may be very fine of about 0.2 microns or less, or large with a projected area diameter of up to about 10 microns, and the emulsions may be poly-disperse emulsions or mono-disperse emulsions.

The photographic emulsion for use in the present invention can be prepared, for example, using the methods disclosed in Research Disclosure (RD) No. 17643 (December, 1978), pages 22 to 23, "I. Emulsion Preparation and Types", and Research Disclosure No. 18716 (November 1979), page 648, by P. Glafkides in Chimie et Physique Photographique , published by Paul Montel, 1967, by G.F. Duffin in Photographic Emulsion Chemistry , published by Focal Press, 1966, and by V.L. Zelikmann et al. in Making and Coating Photographic Emulsions , published by Focal Press, 1964.

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

Furthermore, tabular grains which have an aspect ratio of at least about 5 can be used in the present invention. Tabular grains can be prepared using the methods described, for example, by Gutoff in Photographic Science and Engineering , Volume 14, pages 248 to 257 (1970), an in U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520, and British Patent 2,112,157.

The crystal structure may by uniform, or the interior and exterior parts of the grains may have a different halogen composition, or the grains may have a layer-like structure. Furthermore, silver halides having a different compositions may be joined with an epitaxial junction or they may be joined with compounds other than silver halides, such as silver thiocyanate or lead oxide, for example. Furthermore, mixture of grains which have various crystalline forms can be used.

The above described emulsions may be of the surface latent image type with which the latent image is formed principally on the surface, or of the internal latent image type wherein the latent image is formed within the grains, or of the type wherein the latent image is formed both within the grains and on the grain surface, but a negative type emulsion is required.

The silver halide emulsion of the present invention is generally been subjected to physical ripening, chemical ripening and spectral sensitization. Useful additives for such processes are disclosed, for example, in Research Disclosure Nos. 17643 and 18716, and the locations of these disclosures are summarized in the table below.

Known photographically useful additive which can be used in the present invention are also disclosed in the two Research Disclosure documents noted above, and the locations within these disclosures by type of additive are also indicated in the table below.

Type of Additive	RD 17643	RD 18716
1. Chemical sensitizers	Page 23	Page 648, right col.
2. Speed increasing agents		As above
3. Spectral sensitizers and Super-sensitizers	Pages 23 to 24	Pages 648 right col. to 649 right col.
4. Whiteners	Page 24	
5. Anti-foggants & Stabilizers	Pages 24 to 25	Page 649, right col.
6. Light absorbers, filter dyes and UV absorbers	Pages 25 to 26	Pages 649, right col. to 650, left col.
7. Anti-staining agents	Page 25, right col.	Page 650, left to right cols.
8. Dye image stabilizers	Page 25	
9. Film hardening agents	Page 26	Page 651, left col.
10. Binders	Page 26	As above
11. Plasticizers, lubricants	Page 27	Page 650, right col.
12. Coating promotors, Surfactants	Pages 26 to 27	Page 650, right col.
13 Anti-static agents	Pages 27	As above

Furthermore, the addition of compounds to the photographic material which react with and fix formaldehyde as disclosed in U.S. Patents 4,411,987 and 4,435,503, is desirable for preventing deterioration of photographic performance due to formaldehyde gas.

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

The couplers disclosed, for example, in U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752 and 4,248,961, JP-B-58-10739, British Patents 1,425,020 and 1,467,760, U.S. Patents 3,973,968, 4,314,023 and 4,511,649, and European Patent 249,473A are preferred as yellow couplers.

5-Pyrazolone based compounds and pyrazoloazole based compounds are preferred as magenta couplers, and those disclosed, for example, 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), JP-A-60-33552, Research Disclosure No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654 and 4,556,630, and International Patent WO 88/04795 are especially desirable.

Phenol and naphthol based couplers are useful as cyan couplers, and those disclosed, for example, 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 and 4,327,173, West German Patent Laid Open 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212 and 4,296,199, and JP-A-61-42658 are preferred.

The colored couplers for correcting the unwanted absorptions of colored dyes as disclosed, for example, in section VII-G of Research Disclosure No. 17643, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, and British Patent 1,146,368 are preferred. Furthermore, the use of couplers which correct the unwanted absorption of colored dyes by means of releasing fluorescent dyes which are released on coupling as disclosed in U.S. Patent 4,774,181, and couplers which have, as leaving groups, dye precursors which can form dyes on reaction with the developing agent disclosed in U.S. Patent 4,777,120, aer also desirable.

The couplers disclosed in U.S. patent 4,366,237, British Patent 2,125,570 European Patent 96,570 and West German Patent (Laid Open) 3,234,533 are preferred as couplers, the colored dyes of which have a suitable degree of diffusibility.

Typical examples of polymerized dye forming couplers are disclosed, for example, in U.S Patents 3,451,820, 4,080,211, 4,367,282, 4,409,320 and 4,576,910, and British Patent 2,102,173.

The use of couplers which release photographically useful residual groups on coupling is desirable in the present invention. The DIR couplers which release development inhibitors disclosed in the patents cited in section VII-F of the above noted Research Disclosure 17643, JP-A-57-151944, JP-A-57- 154234, JP-A-60-184248, JP-A-63-37346, JP-A-63-37350 and U.S. Patents 4,248,962 and 4,782,012 are preferred.

The couplers disclosed in British Patents 2,097,140 and 2,131,188, JP-A-59-157638 and JP-A-59-170840 are preferred as couplers which imagewise release nucleating agents or development accelerators during development.

Other compounds which can be used in the photographic photosensitive material of the present invention include the competitive couplers disclosed, for example, in U.S. Patent 4,130,427, the polyequivalent couplers disclosed, for example, in U.S. patents 4,283,472, 4,338,393 and 4,310,618, the DIR redox compound releasing couplers, DIR coupler releasing couplers, DIR coupler releasing redox compounds or DIR redox releasing redox compounds disclosed, for example, in JP-A-60-185950 and JP-A-62-24252, the couplers which release dyes the color of which is restored after elimination as disclosed in European Patents 173,302A and 313,308A, the bleach accelerator releasing couplers as disclosed, for example, in Research Disclosure No. 11449, ibid , No. 24241, and JP-A-61-201247, the ligand releasing couplers as disclosed, for example, in U.S. Patent 4,553,477, the leuco dye releasing couplers as disclosed in JP-A-63-75747, and the couplers which release fluorescent dyes disclosed in U.S. Patent 4,774,181.

The couplers which are used in the present invention can be introduced into the photosensitive material using a variety of known methods of dispersion.

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

Actual examples of high boiling point organic solvents which have a boiling point of at least 175° C at normal pressure for use in the oil in water dispersion method include phthalic acid esters (for example, dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-tert-amylphenyl)-phthalate, bis(2,4-di-tert-amylphenyl)-isophthalate and bis(1,1-diethylpropyl)phthalate), phosphate or phosphonate esters (for example, triphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tri-butoxyethyl phosphate, trichloropropyl phosphate and di-2-ethylhexyl phenyl phosphonate), benzoic acid esters (for example, 2-ethylhexyl benzoate, dodecyl benzoate, 2-ethylhexyl p-hydroxybenzoate), amides (for example, N,N-diethyldodecanamide, N,N-diethyllaurylamide and N-tetradecyl pyrrolidone), alcohols or phenols (for example, isostearyl alcohol and 2,4-di-tert-amylphenol), aliphatic carboxylic acid esters (for example, bis(2-ethylhexyl)sebacate, dioctyl azelate, glycerol tributyrate, isostearyl lactate and trioctyl citrate), aniline derivatives (for example, N,N-dibutyl-2-butoxy-5-tert-octylaniline) and hydrocarbons (for example, paraffins, dodecylbenzene and di-isopropylnaphthalene). Furthermore, organic solvents which have a boiling point above about 30° C, and preferably at least 50° C, but below about 160° C can be used as auxiliary solvents, and typical examples of these solvents include ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate and dimethylformamide.

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

The addition to the color photosensitive materials of the present invention of various fungicides and bactericide such as 1,2-benzisothiazolin-3-one, n-butyl p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol and 2-(4-thiazolyl) benzimidazole as disclosed in JP-A-63-257747, JP-A-62-272248 and JP-A-H1-80941 is preferred.

Suitable supports for use in the present invention have been disclosed, for example, on page 28 of the aforementioned Research Disclosure No. 17643, and from the right hand column of page 647 to the left hand column of page 648 of Research Disclosure No. 18716.

The photographic photosensitive material of the present invention preferably has a total film thickness of all of the hydrophilic colloid layers on the side of the support where the photosensitive emulsion layers are located is not more than 28 μm, more desirably not more than 23 μm, and most desirably not more than 20 µm. Furthermore, the film swelling rate $T_{\frac{1}{2}}$ is preferably not more than 30 seconds and most desirably not more than 20 seconds, Here, the film thickness means the film thickness measured under conditions of 25 °C, 55% relative humidity (2 days), and the film swelling rate $T_{\frac{1}{2}}$ is that measured using methods well known in the art. For example, measurements can be made using a swellometer of the type described by A. Green in Photogr. Sci. Eng. , Volume 19, Number 2, pages 124 to 129, and the swelling rate $T_{\frac{1}{2}}$ is defined as the time taken to reach half the saturated film thickness, taking 90% of the maximum swelled film thickness reached on processing the material for 3 minutes 15 seconds in a color development bath at 30 °C as the saturated film thickness.

The film swelling rate $T_{\frac{1}{2}}$ can be adjusted by adding film hardening agents for the gelatin which is used as a binder, or by changing the ageing conditions after coating. Furthermore, the swelling factor is preferably from 150% to 400%. The swelling factor can be calculated from the maximum swelled film thickness obtained under the conditions described above using the expression (maximum swelled film thickness - film thickness)/film thickness.

The color development baths used in the development processing of photographic photosensitive material of this present invention is preferably an aqueous alkaline solution containing a primary aromatic amine based color developing agent as the principal component. Aminophenol based compounds are also useful as color developing agents, but the use of p-phenylenediamine based compounds is preferred, and typical examples include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-β-methoxyethylaniline, and the sulfate, hydrochloride and p- toluenesulfonate salts of these compounds. Among these compounds, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline sulfate is especially desirable. Two or more of these compounds can be used in combination, according to the particular application.

The color development bath generally contains pH buffers such as alkali metal carbonates, borates or phosphates, and development inhibitors or anti-foggants such as bromides, iodides, benzimidazoles, benzothiazoles or mercapto compounds. They may also contain, as required, various preservatives such as hydroxylamine, diethylhydroxylamine, sulfites, hydrazines such as N,N-biscarboxymethylhydrazine, phenylsemicarbazides, triethanolamine and catecholsulfonic acids, organic solvents such as ethylene glycol and diethylene glycol, development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts and amines, dye forming couplers, competitive couplers, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, thickeners and various chelating agents as typified by the aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, typical examples of which include ethylenediamine tetra-acetic acid, nitrilotriacetic acid, diethylenetriamine penta-acetic acid, cyclohexanediamine tetra-acetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N,N-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid) and salts of these acids.

The processing baths other than the color development bath and the processing operation for color reversal photographic photosensitive material of the present invention are described below.

Processing from black and white development through to color development in the processing operations for the color reversal photographic photosensitive material of this present invention can be carried out as follows:

1) Black and white development - water wash - reversal - color development
2) Black and white development - water wash - light reversal - color development
3) Black and white development - water wash - color development

The water wash in processes 1) to 3) can be replaced by a rinse process as disclosed in U.S. Patent 4,804,616 with a view to simplifying processing and reducing the amount of effluent.

The processes following color development are described below:

4) Color development - conditioning - bleaching -fixing - water washing - stabilization
5) Color development - water washing - bleaching -fixing - water washing - stabilization
6) Color development - conditioning - bleaching - water washing - fixing - water washing - stabilization
7) Color development - water washing - bleaching -water washing - fixing - water washing -stabilization
8) Color development - bleaching - fixing - water washing - stabilization
9) Color development - bleaching - bleach-fixing -water washing - stabilization
10) Color development - bleaching - bleach-fixing -fixing - water washing - stabilization
11) Color development - bleaching - water washing -fixing - water washing - stabilization
12) Color development - conditioning - bleach-fixing -water washing - stabilization
13) Color development - water washing - bleach-fixing -water washing - stabilization
14) Color development - bleach-fixing - water washing -stabilization
15) Color development - fixing - bleach-fixing - water washing - stabilization

The water washing process immediately preceding the stabilization process may be omitted in processing operations 4) to 15), or conversely the final stabilization process may be omitted. The color reversal processing operation is established by combining any one of the above described processing operations 1) to 3) with any one of the processing operations 4) to 15).

The processing baths used for the color reversal processing operations in this present invention are described below.

Known black and white developing agents can be used in the black and white processing baths for use in processing the photographic material of the present invention. Thus, dihydroxybenzenes (for example hydroquinones, 3-pyrazolidones (for example, 1-phenyl-3-pyrazolidones, aminophenols (for example, N-methyl-p-aminophenol), 1-phenyl-3-pyrazolines, ascorbic acid and the heterocyclic compounds derived by condensing a 1,2,3,4-tetrahydroquinoline ring with an indolene ring disclosed in U.S. Patent 4,067,872, for example, can be used either individually or in combinations for the developing agent.

Preservatives (for example, sulfite, bisulfite), buffers (for example, carbonate, boric acid, borate, alkanolamine), alkalis (for example, hydroxides, carbonate), dissolution promotors (for example, polyethylene glycols and esters thereof), pH adjusting agents (for example, organic acids such as acetic acid), sensitizers (for example, quaternary ammonium salts), development accelerators, surfactants, anti-foaming agents, film hardening agents, and viscosity imparting agents, for example, may be included in the black and white development bath for use in the present invention. Compounds which act as silver halide solvents must be included in the black and white development bath for use in the present invention, but generally the sulfite which is added as a preservative as described above is satisfactory as the silver halide solvent. Sulfites and other silver halide solvents which can be used include, for example, KSCN, NaSCN, K_2SO_3, Na_2SO_3, $K_2S_2O_5$, $Na_2S_2O_5$, $K_2S_2O_3$ and $Na_2S_2O_3$.

The pH value of the black and white development bath adjusted to provide the desired density and contrast, preferably being within the range from about 8.5 to about 11.5.

The development time may be prolonged for up to a maximum of three times the standard processing time for push-processing using the black and white development bath. The prolongation of the development time for push processing can be shortened by raising the processing temperature.

The pH of the color development baths and black and white developing bath for use in the present invention is generally from 9 to 12. Furthermore, the replenishment rate for the development baths depends on the color photographic photosensitive material being processed, but is generally not more than 3 liters per square meter of photosensitive material and can be set to not more than 500 ml by reducing the bromide ion concentration in the replenisher. Where the replenishment rate is low, it is desirable that evaporation and aerial oxidation of the liquid is reduced by minimizing the area of contact with the air in the processing tank.

The contact area between the air and the photographic processing bath in a processing tank can be represented by the open factor which is defined below. Thus:

$$\text{Open Factor} = \frac{\text{Processing bath and Air Contact Area (Cm}^2\text{)}}{\text{Processing Bath Volume (cm}^3\text{)}}$$

The above described open factor is preferably 0.1 or less, and most desirably from 0.001 to 0.05. In addition to providing a shielding material such as a floating lid, for example, on the surface of the photographic processing bath in the processing tank, the method employing a movable lid as disclosed in JP-A-H1-82033 and the method involving the slit development processing disclosed in JP-A-63-216050 can be used as means of reducing the open factor. Reduction of the open factor is preferably applied not only to the processes of color development and black and white development but also to all the subsequent processes, such as the bleaching, bleach-fixing, fixing, water washing and stabilization processes. Furthermore, the replenishment rate can be reduced by using means for suppressing the accumulation of bromide ion in the development bath.

Known fogging agents can be included in the reversal baths which are used after black and white development. Namely, use can be made of stannous ion complex salts such as stannous ion - organophosphoric acid complex salts (U.S. Patent 3,617,282), stannous ion - organophosphonocarboxylic acid complex salts (JP-B-56-32616) and stannous ion - aminopolycarboxylic acid complex salts (U.S. Patent 1,209,050), and boron compounds such as borohydride compounds (U.S. Patent 2,984,567) and heterocyclic amine borane compounds (British Patent 1,011,000). The pH of the fogging bath (reversal bath) can be set within a wide range from the acid side to the alkaline side, ranging from pH 2 to pH 12, preferably from pH 2.5 to pH 10, and most desirably from pH 3 to pH 9. A light reversal process with re-exposure to light can be used instead of a reversal bath, and the reversal process can be omitted by adding the above described fogging agent to the color development bath.

The silver halide color photographic photo-sensitive material of the present invention is subjected to a bleaching process or a bleach-fixing process after color development. These processes can be carried out immediately after color development without any intervening processes, or the bleaching process or bleach-fixing process can be carried out after a post color development, stop, conditioning or water washing process, for example, in order to prevent unwanted after-development and aerial fogging, to reduce the carry-over of color development bath into the de-silvering process, to wash-out the sensitive material components such as the sensitizing dyes and dyes, etc. included in the photographic photosensitive material and the developing process agents which have been impregnated into the photographic photosensitive material, and to prevent the occurrence of contamination.

The photographic emulsion layer is subjected to a conventional bleaching process after color development. The bleaching process may be carried out at the same time as the fixing process (in a bleach-fix process) or it may be carried out as a separate process. Moreover, a bleach-fix process can be carried out after a bleaching process in order to speed up processing. Moreover, processing can be carried out in two connected bleach-fix baths, a fixing process can be carried out before a bleach-fixing process or a bleaching process can be carried out after a bleach-fix process, as required. Compounds of multi-valent metals, such as iron(III) for example, peracids, quinones and nitro compounds can be used as the bleaching agent. Typical bleaching agents include organic complex salts of iron(III), for example complex salts with aminopolycarboxylic acids such as ethylenediamine tetra-acetic acid, diethylenetriamine penta-acetic acid, cyclohexanediamine tetra-acetic acid, methylimino diacetic acid, 1,3-diaminopropane tetra-acetic acid and glycol ether diamine tetra-acetic acid, or citric acid, tartaric acid or malic acid. From among these bleaching agents, the use of polyaminocarboxylic acid iron(III) complex salts, principally ethylenediamine tetra-acetic acid iron(III) complex salts and 1,3-diaminopropane tetra-acetic acid iron(III) salts, is preferred for both rapid processing and the prevention of environmental pollution. Moreover, the aminopolycarboxylic acid iron(III) complex salts are especially useful in both bleach baths and bleach-fix baths. The pH value of the bleach baths and bleach-fix baths in which these aminopolycarboxylic acid iron(III) salts are used is generally from 4.0 to 8, but lower pH values can be used in order to speed up processing.

Bleaching accelerators can be used, as required, in the bleach baths, bleach-fix baths or bleach or bleach-fix pre-paths. Examples of useful bleach accelerators are disclosed in the following patent publications, including compounds having a mercapto group or a disulfide group as disclosed, for example, in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426, and Research Disclosure No. 17129 (June 1978); thiazolidine derivatives as disclosed in JP-A-50-140129; thiourea derivatives as disclosed in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735 and U.S. Patent 3,706,561, iodides as disclosed in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds as disclosed in West German Patents 966,410 and 2,748,430; polyamine compounds as disclosed in JP-B-45-8836; other compounds as disclosed in JP-A-49-42434, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506 and JP-A-58-163940; and the bromide ion. From among the above compounds, those having a mercapto group or a disulfide group are preferred in view of their large accelerating effect, and the compounds disclosed in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 are especially desirable. Moreover, the compounds disclosed in U.S. patent 4,552,834 are also desirable. The above noted bleaching accelerators may also be added to the photographic photosensitive material. The bleaching accelerators are especially effective for use in bleach-fixing camera color photographic photosensitive materials.

The inclusion of organic acids as well as the compounds indicated above in the bleach baths and bleach-fixing baths is desirable for preventing the occurrence of bleach staining. Compounds which have an acid dissociation constant (pKa) of from 2 to 5 are especially desirable as organic acids, and useful examples include acetic acid and propionic acid.

Thiosulfates, thiocyanates, thioether based compounds, thioureas and large amounts of iodide can be used, for example, as the fixing agent which is used in a fixing bath or bleach-fix bath, but thiosulfates are generally used and ammonium thiosulfate in particular can be used in the widest range of applications. Furthermore, the combined use of thiosulfate and thiocyanate, thioether compounds, thiourea etc. is also desirable. Sulfites, bisulfites, carbonyl/bisulfite addition compounds or the sulfinic acid compounds disclosed in European Patent 294769A are preferred as preservatives for fixing baths and bleach-fix baths. Moreover, the addition of various aminopolycarboxylic acids and organophosphonic acids to the fixing baths and bleach-fixing baths is desirable for stabilizing the baths. The total time of the de-silvering process is preferably as short as possible within the range where de-silvering failure does not occur. The preferred de-silvering time is from 1 to 3 minutes, and most desirably the de-silvering time is from 1 to 2 minutes. Furthermore, the processing temperature is from 25° C to 50° C, and preferably from 35° C to 45° C. The de-silvering rate is improved and the occurrence of staining after processing is effectively prevented within the preferred temperature range.

The de-silvering baths are preferably agitated as strongly as possible during the de-silvering process. Agitation methods include methods in which a jet of the processing bath is directed onto the emulsion surface of the photosensitive material as disclosed in JP-A-62-183460 and JP-A-62-183461, methods in which the agitation effect is increased using a rotary device as disclosed in JP-A-62-183461, methods in which the photosensitive material is moved while in contact with a wiper blade which is established in the bath and the agitation effect is increased by the generation of turbulence at the emulsion surface, and methods in which the circulating flow rate of the processing bath as a whole is increased. The above described means of increasing agitation are effective in bleach baths, bleach-fix baths and fixing baths. It is considered that increased agitation increases the rate of supply of bleaching agent and fixing agent to the emulsion film to thereby increases the de-silvering rate. Furthermore, the above described means for increasing agitation are more effective in cases where a bleaching accelerator is used, and may provide a marked increase in the accelerating effect and eliminate the fixer inhibiting action of the bleaching accelerator.

The automatic processors which can be used for processing the photographic photosensitive material of the present invention preferably employs photosensitive material transporting devices as disclosed in JP-A-60-191257, JP-A-60-191258 and JP-A-60-191259. With a transporting device, such as that disclosed in the above noted JP-A-60-191257, the carry over of processing bath from one bath to the next bath is greatly reduced and this is very effective for preventing deterioration in processing bath performance. These effects are especially useful for shortening the processing time in each process and for reducing the replenishment rate of each processing bath.

The silver halide color photographic photo-sensitive material of the present invention is generally subjected to a water washing process and/or stabilization process after the de-silvering process. The amount of wash water used in the washing process can be set within a wide range, depending on the application and the nature of the photographic photosensitive material (e.g., type of couplers contained therein), the wash water temperature, the number of water washing tanks (the number of water washing stages) and the replenishment system, e.g., whether a counter flow or a sequential flow system is used, and various other conditions. The relationship between the amount of water used and the number of washing tanks in a multi-stage counter-flow system can be obtained using the method described at pages 248 to 253 of the Journal of the Society of Motion Picture and Television Engineers , Volume 64 (May 1955).

The amount of wash water used can be greatly reduced by using a multi-stage counter-flow system noted in the above described literature, but bacteria proliferate due to the increased residence time of the water in the tanks, and problems arise with the suspended matter which is produced and which attaches to the photographic photosensitive material. The method in which the calcium ion and magnesium ion concentrations are reduced, as disclosed in JP-A-62-288838, is very effective as a means of overcoming this problem when processing the color photographic photosensitive material of the present invention. Furthermore, the isothiazolone compounds and thiabendazoles disclosed in JP-A-57-8547, the chlorine based disinfectants such as chlorinated sodium isocyanurate, and benzotriazole, for example, and the disinfectants disclosed in The Chemistry of Biocides and Fungicides by Horiguchi, (1986, Sanko Shuppan), in Killing Micro-organisms, Biocidal and Fungicidal Techniques (1982) published by the Health and Hygiene Technology Society, and in A Dictionary of Biocides and Fungicides (1986) published by the Japanese Biocide and Fungicide Society, can also be used for the purpose.

The pH value of the washing water used to process the photographic photosensitive material of the present invention is from 4 to 9, and preferably from 5 to 8. The washing water temperature and the washing time is set depending on the nature and application of the photographic photosensitive material but, in general, washing conditions of from 20 seconds to 10 minutes at a temperature of from 15° C to 45° C and preferably from 30 seconds to 5 minutes at a temperature of from 25° C to 40° C, are selected. Moreover, the photographic photosensitive material of the present invention can be processed directly in a stabilizing bath instead of being subjected to a water wash as described above. The known methods disclosed in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345 can be used for a stabilization process of this type.

Furthermore, in some cases a stabilization process is carried out following the above described water washing process, and a stabilizing bath containing a dye stabilizing agent and surfactant used as the final bath with a camera color photographic photosensitive material is an example of such a process. Aldehydes such as formalin and glutaraldehyde, N-methylol compounds, hexamethylenetetramine and aldehyde/bisulfite addition compounds can be used, for example, as the dye stabilizing agent.

Various chelating agents and fungicides can also be added to the stabilizing baths.

The overflow which accompanies replenishment of the above described water washing or stabilizing bath can be reused in other processes, such as the de-silvering process for example.

Concentration correction with the addition of water is desirable in cases where the above described processing baths are concentrated by evaporation when processing in an automatic processor, for example.

Color developing agents can be incorporated into the silver halide color photographic photosensitive material of the present invention in order to simplify and to speed up processing. The incorporation of various color developing agent precursors is preferred. For example, the indoaniline based compounds disclosed in U.S. Patent 3,342,597, the Shiff's base type compounds disclosed in U.S. Patent 3,342,599, Research Disclosure No. 14850 and ibid , No. 15159, the aldol compounds disclosed in Research Disclosure No. 13924, the metal complex salts disclosed in U.S. Patent 3,719,492 and the urethane based compounds disclosed in JP-A-53-135628 can be used for this purpose.

Various 1-phenyl-3-pyrazolidones may be incorporated, as required, into the silver halide color photographic photosensitive material of the present invention in order to accelerate color development. Typical compounds are disclosed, for example, in JP-A-56-64339, JP-A-57-144547 and JP-A-58-115438.

The various processing baths in the present invention are used at a temperature of from 10°C to 50°C. The standard temperature is generally from 33°C to 38°C, but accelerated processing and shorter processing times can be realized at higher temperatures while, on the other hand, increased picture quality and better processing bath stability is achieved at lower temperatures. Furthermore, processes using hydrogen peroxide intensification or cobalt intensification as disclosed in West German Patent 2,226,770, or U.S. Patent 3,674,499 can be used in order to economize on the silver contained in the photographic photosensitive material.

ILLUSTRATIVE EXAMPLES

The present invention is described below by reference to the following illustrative examples, but the invention is not to be construed as being limited by these examples.

EXAMPLE 1

Preparation of Sample 101

A multi-color photosensitive material comprising each of the layers having the composition indicated below was prepared on a cellulose triacetate film support having a thickness of 127 μm on which a subbing layer had been established. The numerical values indicate the amount added in grams per square meter of the photosensitive material, unless otherwise noted. Moreover, the effects of the constituent compounds added are not limited to the application disclosed.

First Layer Anti-halation Layer	
Black colloidal silver	0.25
Gelatin	1.9
Ultraviolet absorber U-1	0.04
Ultraviolet absorber U-2	0.1
Ultraviolet absorber U-3	0.1
Ultraviolet absorber U-6	0.1
High boiling point organic solvent Oil-1	0.1

Second Layer Intermediate Layer	
Gelatin	0.40

Third Layer Intermediate Layer	
Fogged fine grain silver iodobromide emulsion (average grain size 0.06 µm, AgI content 1 mol%)	as silver 0.05
Gelatin	0.4

Fourth Layer Low Speed Red Sensitive Emulsion Layer

Silver iodobromide emulsion (a 1 : 1 mixture of a monodisperse cubic emulsion of average grain size 0.4 µm, AgI content 4.5 mol%, and a monodisperse emulsion of average grain size 0.3 µm, AgI content 4.5 mol%) which had been spectrally sensitized with the sensitizing dyes S-1 and S-2	as silver 0.4
Gelatin	0.8
Coupler C-1	0.20
Coupler C-9	0.05
High boiling point organic solvent Oil-2	0.10

Fifth Layer Medium Speed Red Sensitive Emulsion Layer	
Silver iodobromide emulsion (a mono-disperse cubic emulsion of average grain size 0.5 µm and AgI content 4 mol%) which had been spectrally sensitized with the sensitizing dyes S-1 and S-2	as silver 0.4
Gelatin	0.8
Coupler C-1	0.2
Coupler C-2	0.05
Coupler C-3	0.2
High boiling point organic solvent Oil-2	0.1

Sixth Layer High Speed Red Sensitive Emulsion Layer	
Silver iodobromide emulsion (a mono-disperse twinning grains emulsion of average grain size 0.7 µm and AgI content 2 mol%) which had been spectrally sensitized with the sensitizing dyes S-1 and S-2	as silver 0.4
Gelatin	1.1
Coupler C-3	0.7
Coupler C-1	0.3

Seventh Layer Intermediate Layer	
Gelatin	0.6
Dye D-1	0.02

Eighth Layer Intermediate Layer	
Fogged silver iodobromide emulsion (average grain size 0.06 µm. AgI content 0.3 mol%)	as silver 0.02
Gelatin	1.0
Anti-color mixing agent Cpd-1	0.2

Ninth Layer Low Speed Green Sensitive Emulsion Layer

Silver iodobromide emulsion (a 1 : 1 mixture of a monodisperse cubic emulsion of average grain size 0.4 µm, AgI content 4.5 mol%, and a monodisperse emulsion of average grain size 0.2 µm. AgI content 4.5 mol%) which had been spectrally sensitized with the sensitizing dyes S-3 and S-4	as silver 0.5
Gelatin	0.5
Coupler C-4	0.20
Coupler C-7	0.10
Coupler C-8	0.10
Compound Cpd-B	0.03
Compound Cpd-E	0.02
Compound Cpd-F	0.02
Compound Cpd-G	0.02
Compound Cpd-H	0.02
Compound Cpd-D	0.01
High boiling point organic solvent Oil-1	0.1
High boiling point organic solvent Oil-2	0.1

Tenth Layer Intermediate Speed Green Sensitive Emulsion Layer	
Silver iodobromide emulsion (a mono-disperse cubic emulsion of average grain size 0.5 µm, AgI content 3 mol%) which had been spectrally sensitized with the sensitizing dyes S-3 and S-4	as silver 0.4
Gelatin	0.6
Coupler C-4	0.1
Coupler C-7	0.1
Coupler C-8	0.1
Compound Cpd-B	0.03
Compound Cpd-E	0.02
Compound Cpd-F	0.02
Compound Cpd-G	0.05
Compound Cpd-H	0.05
High boiling point organic solvent Oil-2	0.01

Eleventh Layer High Speed Green Sensitive Emulsion Layer	
Silver iodobromide emulsion (a mono-disperse tabular emulsion of average grain size (calculated as a sphere) 0.6 µm, AgI content 1.3 mol%, average diameter/thickness value 7) which had been spectrally sensitized with the sensitizing dyes S-3 and S-4	as silver 0.5
Gelatin	1.0
Coupler C-4	0.4
Coupler C-7	0.2
Coupler C-8	0.2
Compound Cpd-B	0.08
Compound Cpd-E	0.02
Compound Cpd-F	0.02
Compound Cpd-G	0.02
Compound Cpd-H	0.02
High boiling point organic solvent Oil-1	0.02
High boiling point organic solvent Oil-2	0.02

Twelfth Layer Intermediate Layer	
Gelatin	0.6
Dye D-2	0.05

Thirteenth Layer Yellow Filter Layer	
Yellow colloidal silver	as silver 0.1
Gelatin	1.1
Anti-color mixing agent Cpd-A	0.01
High boiling point organic solvent Oil-1	0.01

Fourteenth Layer Intermediate Layer	
Gelatin	0.6

Fifteenth Layer Low Speed Blue Sensitive Emulsion Layer

Silver iodobromide emulsion (a 1 : 1 mixture of a mono-disperse cubic emulsion of average grain size 0.4 μm, AgI content 3 mol%, and a mono-disperse emulsion of average grain size 0.2 μm. AgI content 3 mol%) which had been spectrally sensitized with the sensitizing dyes S-5 and S-6	as silver 0.6
Gelatin	0.8
Coupler C-5	0.6
High boiling point organic solvent Oil-2	0.02

Sixteenth Layer Intermediate Speed Blue Sensitive Emulsion Layer	
Silver iodobromide emulsion (a mono-disperse cubic emulsion of average grain size 0.5 µm, AgI content 2 mol%) which had been spectrally sensitized with the sensitizing dyes S-5 and S-6	as silver 0.4
Gelatin	0.9
Coupler C-5	0.3
Coupler C-6	0.3
High boiling point prganic solvent Oil-2	0.02

Seventeenth Layer High Speed Blue Sensitive Emulsion Layer

Silver iodobromide emulsion (tabular grains of grain size calculated as a sphere 0.7 µm, AgI content 1.5 mol%, average diameter/thickness value 7) which had been spectrally sensitized with the sensitizing dyes S-5 and S-6	as silver 0.4
Gelatin	1.2
Coupler C-6	0.7

Eighteenth Layer First Protective Layer	
Gelatin	0.7
Ultraviolet absorber U-1	0.04
Ultraviolet absorber U-3	0.03
Ultraviolet absorber U-4	0.03
Ultraviolet absorber U-5	0.05
Ultraviolet absorber U-6	0.05
High boiling point organic solvent Oil-1	0.02
Formalin scavenger Cpd-C	0.8
Dye D-3	0.05

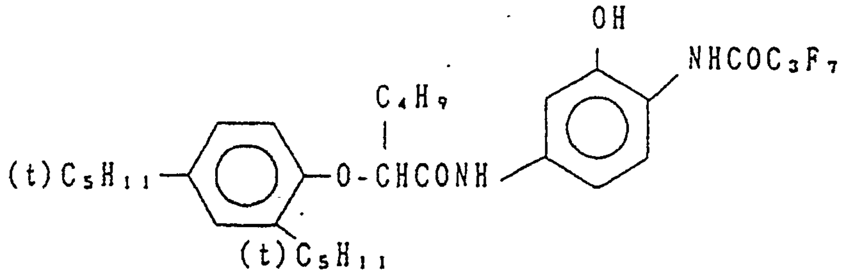
Nineteenth Layer Second Protective Layer	
Fogged fine grained silver iodobromide emulsion (average grain size 0.06 µm, AgI content 1 mol%)	as silver 0.1
Gelatin	0.4

Twentieth Layer Third Protective Layer	
Gelatin	0.4
Poly(methyl methacrylate) (average particle diameter 1.5 µm)	0.1
4 : 6 methyl methacrylate : acrylic acid copolymer (average particle size 1.5 µm)	0.1
Silicone oil	0.03
Surfactant W-1	3.0 mg

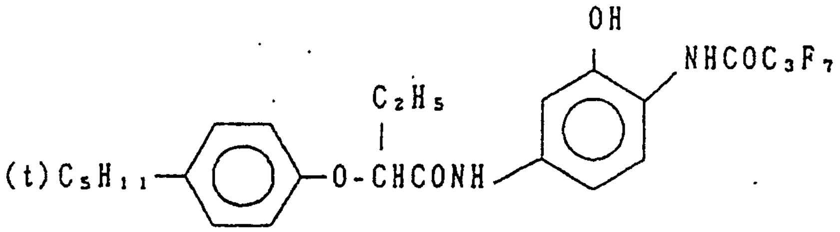
The gelatin film hardening agent H-1 and surfactants for coating and emulsification purposes were also added to each layer in addition to the components indicated above.

Moreover, in the emulsions described here, the term "mono-dispersion" that the variation coefficient is not more than 20%.

C − 1


OH
NHCOC₃F₇
C₄H₉
(t)C₅H₁₁
O-CHCONH
(t)C₅H₁₁

C − 2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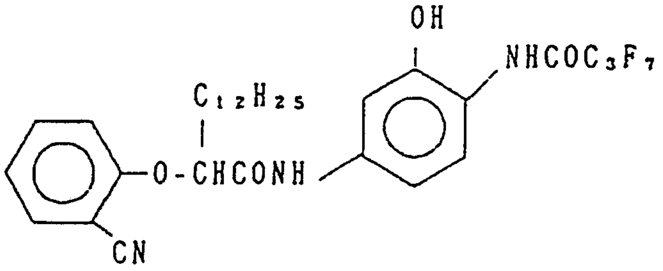
C₂H₅
(t)C₅H₁₁
O-CHCONH

C − 3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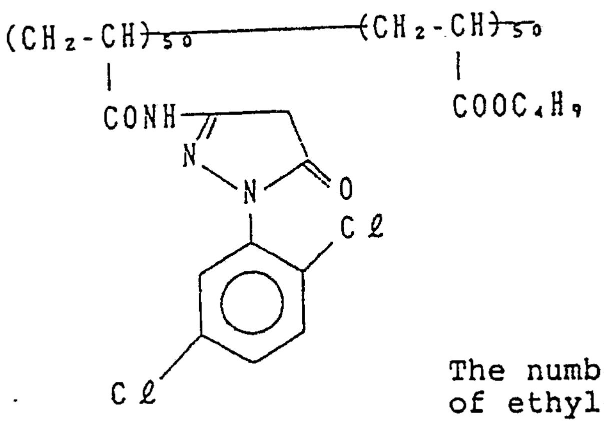
C₁₂H₂₅
O-CHCONH
CN

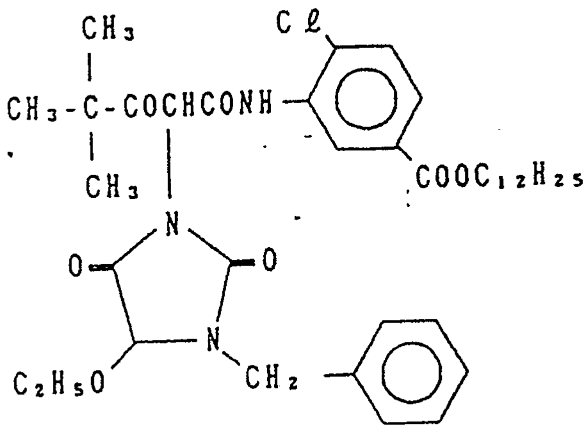
C - 4



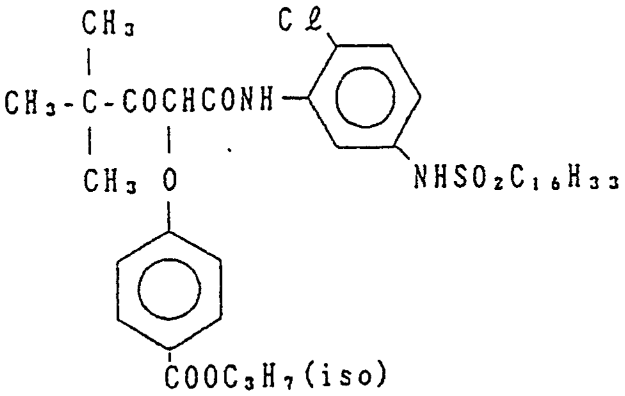
The number indicates wt% of ethylene moiety.

Average molecular weight: About 25,000

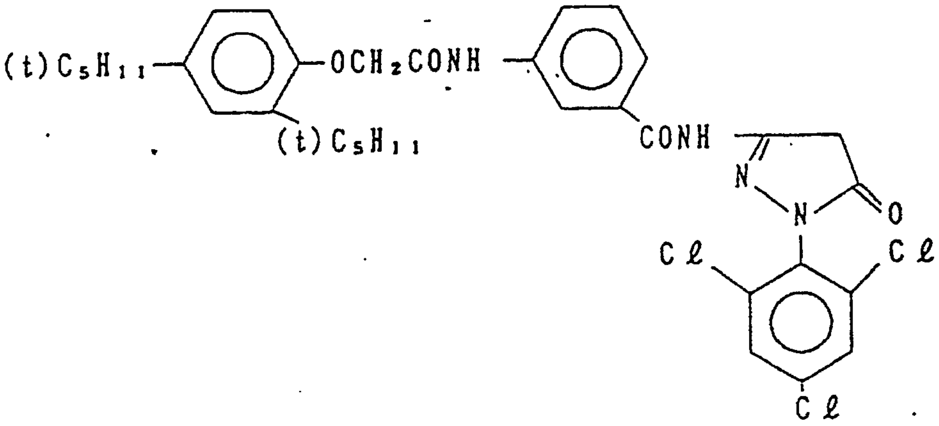
C - 5



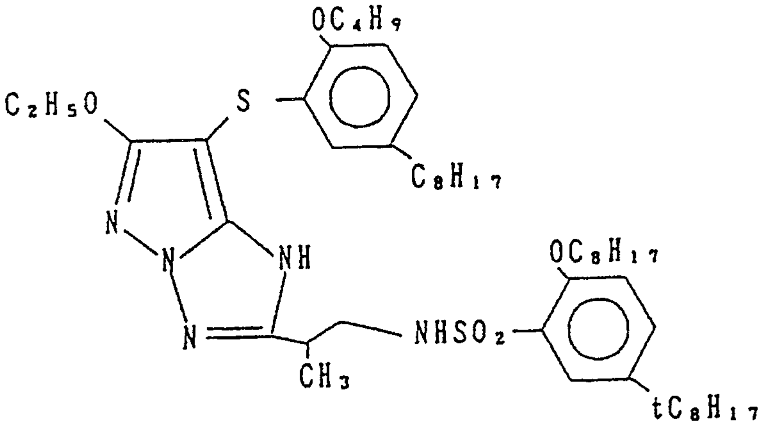
C - 6


CH3
CH3-C-COCHCONH
CH3
O
Cℓ
NHSO2C16H33
COOC3H7(iso)

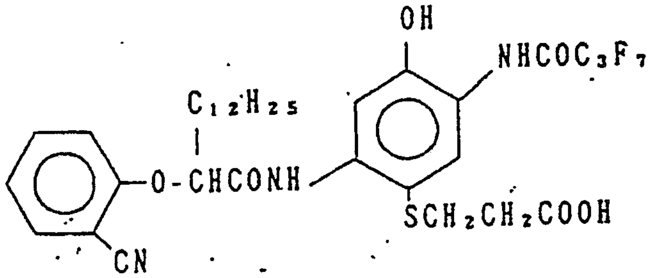
C - 7


(t)C5H11
OCH2CONH
(t)C5H11
CONH
N
N
O
Cℓ
Cℓ
Cℓ

C − 8



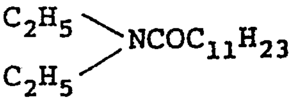
C − 9



Oil-1 Dibutyl phthalate

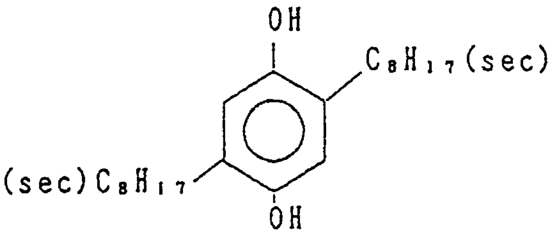
Oil-2 Tricresyl phosphate

Oil-3

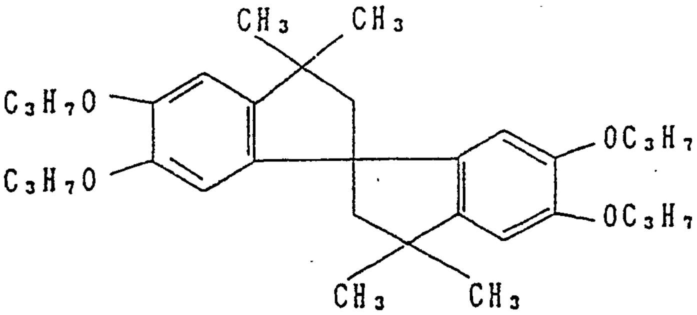


$$(C_2H_5)_2NCOC_{11}H_{23}$$

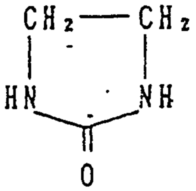
Cpd－A



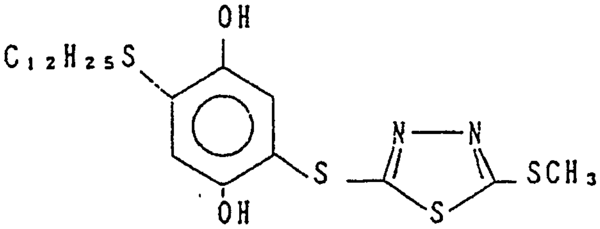
Cpd－B



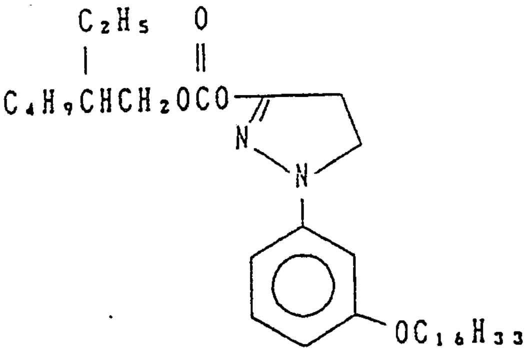
Cpd－C



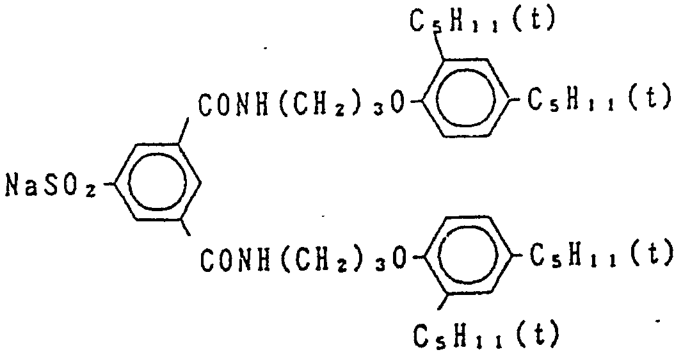
Cpd－D



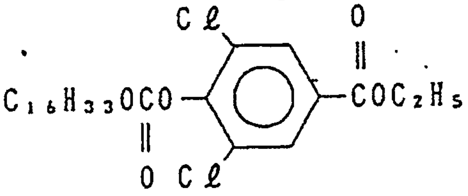
Cpd－E



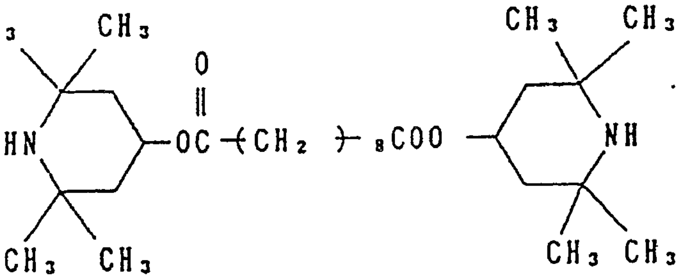
Cpd－F



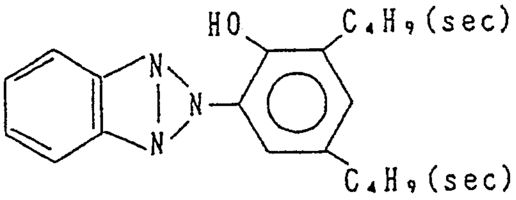
Cpd－G



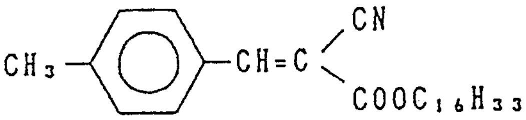
Cpd－H



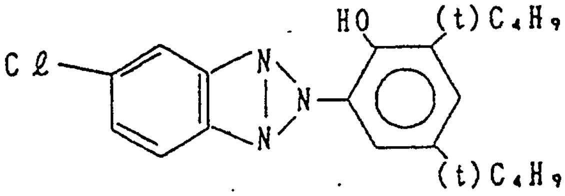
U－1


HO
C₄H₉(sec)
N
N
N
C₄H₉(sec)

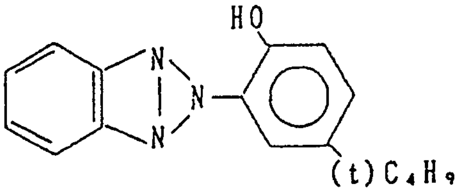
U－2


CH₃
CH=C
CN
COOC₁₆H₃₃

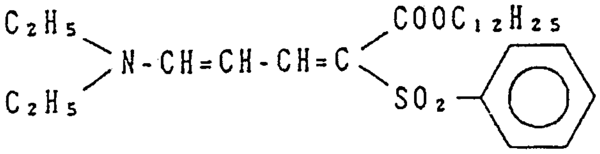
U－3


Cℓ
N
N
N
HO
(t)C₄H₉
(t)C₄H₉

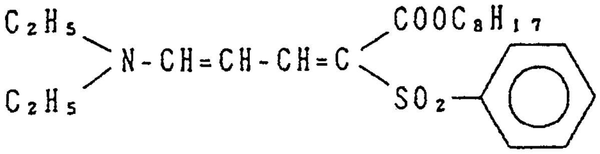
U－4


HO
N
N
N
(t)C₄H₉

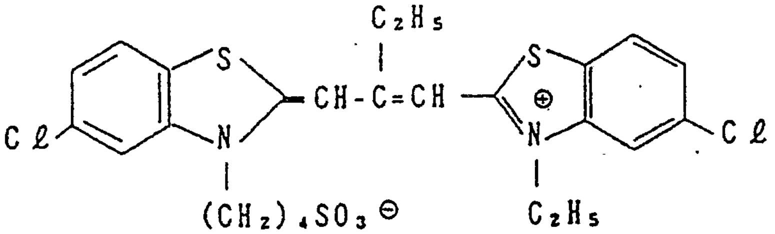
U − 5



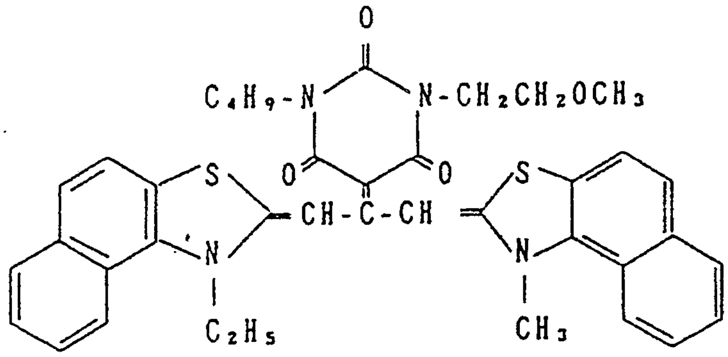
U − 6



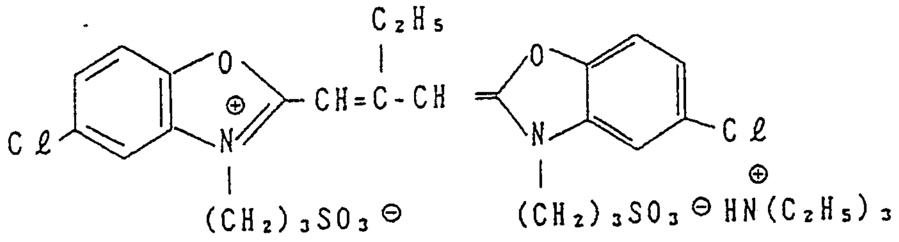
S − 1



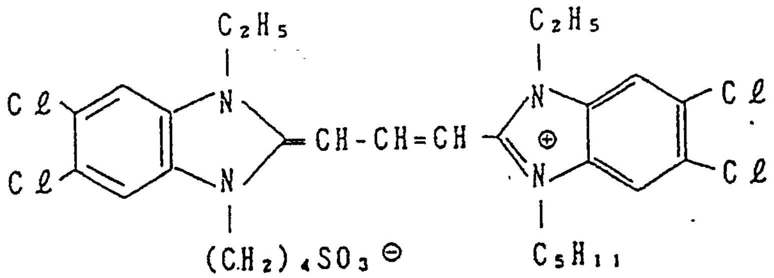
S − 2



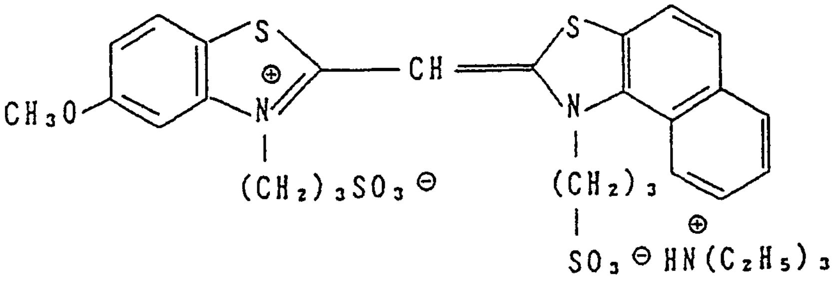
S - 3



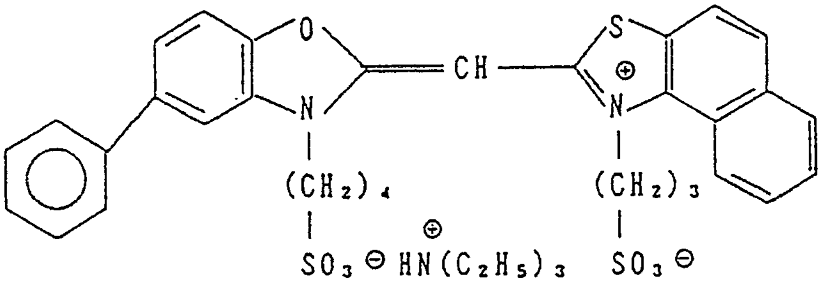
S - 4



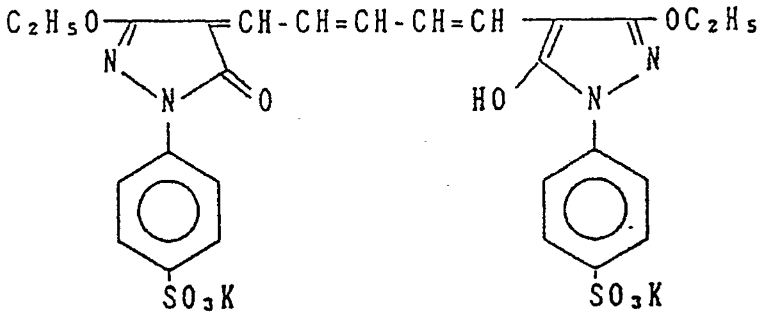
S - 5



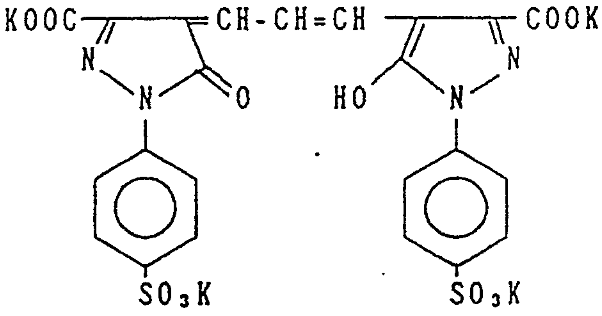
S－6



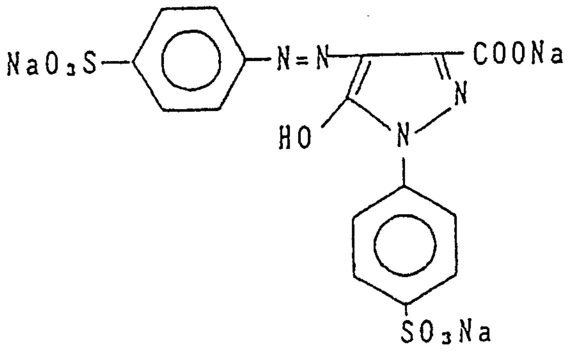
D－1



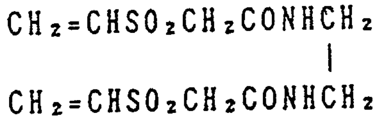
D－2



D – 3

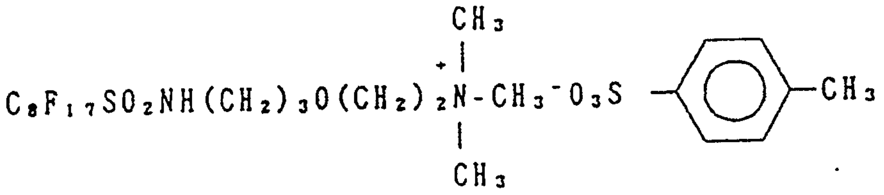


H – 1



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

W – 1



Processing Operation	Time	Temperature	Tank Capacity	Replenishment Rate
Black and white development	6 minutes	38 °C	12 liters	2.2 ℓ/m^2
First water wash	2 minutes	38 °C	4 liters	7.5 ℓ/m^2
Reversal	2 minutes	38 °C	4 liters	1.1 ℓ/m^2
Color development	6 minutes	38 °C	12 liters	2.2 ℓ/m^2
Conditioning	2 minutes	38 °C	4 liters	1.1 ℓ/m^2
Bleaching	6 minutes	38 °C	12 liters	0.22 ℓ/m^2
Fixing	4 minutes	38 °C	8 liters	1.1 ℓ/m^2
Second water wash	4 minutes	38 °C	8 liters	7.5 ℓ/m^2
Stabilization	1 minute	25 °C	2 liters	1.1 ℓ/m^2

The composition of each processing bath was as follows:

Black and White Development

	Parent Bath	Replenisher
Nitrilo-N,N,N-trimethylene-phosphonic acid, penta-sodium salt	2.0 grams	2.0 grams
Sodium sulfite	30 grams	30 grams
Potassium hydroquinone-mono-sulfate	20 grams	20 grams
Potassium carbonate	33 grams	33 grams
1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	2.0 grams	2.0 grams
Potassium bromide	2.5 grams	1.4 grams
Potassium thiocyanate	1.2 grams	1.2 grams
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.

Reversal Bath

	Parent Bath	Replenisher
Nitrilo-N,N,N-trimethylene-phosphonic acid, penta-sodium salt	3.0 grams	Same as the Parent Bath
Stannous chloride, dihydrate	1.0 gram	
p-Aminophenol	0.1 gram	
Sodium hydroxide	8 grams	
Glacial acetic acid	15 ml	
Water to make	1000 ml	
pH	6.00	

The pH was adjusted with hydrochloric acid or sodium hydroxide.

Color Development Bath

	Parent Bath	Replenisher
Nitrilo-N,N,N-trimethylene-phosphonic acid, penta-sodium salt	2.0 grams	2.0 grams
Sodium sulfite	7.0 grams	7.0 grams
Trisodium phosphate dodecahydrate	36 grams	36 grams
Potassium bromide	1.0 gram	-
Potassium bromide	99 mg	-
Sodium hydroxide	3.0 grams	3.0 grams
Citrazinic acid	1.5 grams	1.5 grams
N-Ethyl-(β-methanesulfonamido ethyl)-3-methyl-4-aminoaniline sulfate	11 grams	11 grams
3,6-Dithia-1,8-octanediol	1.0 gram	1.0 gram
Water to make	1000 ml	1000 ml
pH	11.80	12.00

The pH was adjusted with hydrochloric acid or potassium hydroxide.

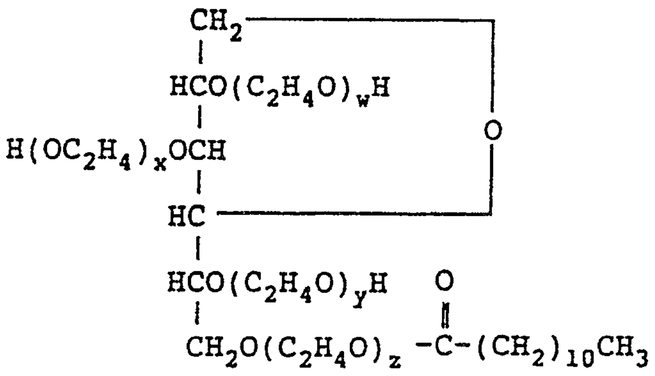
Conditioner		
	Parent Bath	Replenisher
Ethylenediamine tetra-acetic acid, di-sodium salt, di-hydrate	8.0 grams	Same as the Parent Bath
Sodium sulfite	12 grams	
1-Thioglycerine	0.4 ml	
Sorbitan ester*	0.1 gram	
Water to make	1000 ml	
pH	6.20	
The pH was adjusted with hydrochloric acid or sodium hydroxide.		

Bleach Bath		
	Parent Bath	Replenisher
Ethylenediamine tetra-acetic acid, di-sodium salt, di-hydrate	2.0 grams	4.0 grams
Ethylenediamine tetra-acetic acid, Fe(III) ammonium salt, di-hydrate	120 grams	240 grams
Potassium bromide	100 grams	200 grams
Ammonium nitrate	10 grams	20 grams
Water to make	1000 ml	1000 ml
pH	5.70	5.50
The pH was adjusted with hydrochloric acid or sodium hydroxide.		

Fixer bath		
	Parent Bath	Replenisher
Ammonium thiosulfate	8.0 grams	Same as the Parent Bath
Sodium sulfite	5.0 grams	
Sodium bisulfite	5.0 grams	
Water to make	1000 ml	
pH	6.60	
The pH was adjusted with hydrochloric acid or sodium hydroxide.		

Stabilizer Bath		
	Parent Bath	Replenisher
Formalin (37 wt%)	5.0 ml	Same as the Parent Bath
Polyoxyethylene p-monononyl phenyl ether (average degree of polymerization 10)	0.5 ml	
Water to make	1000 ml	
pH	Not adjusted	

Sorbitan Ester*



(w+x+y+z=20)

Samples 102 to 130 were prepared by modifying the layers in sample 101 as shown in Table 1.

TABLE 1 Samples

	First Layer The Black Colloidal Silver	Second Layer In the Intermediate Layer	Fourth Layer In The Low Speed Red Sensitive Emulsion Layer	Ninth Layer In the Low Speed Green Sensitive Emulsion Layer	Thirteenth Layer The Black Colloidal Silver
102	Unchanged	Compound VII-51 10 mg/m^2	Unchanged	Unchanged	Unchanged
103	Unchanged	Unchanged	Compound VII-51 10 mg/m^2	Unchanged	Unchanged
104	Unchanged	Unchanged	Compound VII-51 10 mg/m^2	Compound VII-51 10 mg/m^2	Unchanged
105	Unchanged	Compound VII-1 10 mg/m^2	Unchanged	Compound VII-1 10 mg/m^2	Unchanged
106	Unchanged	Unchanged	Compound VII-2 10 mg/m^2	Compound VII-2 10 mg/m^2	Unchanged
107	Unchanged	Unchanged	Compound VII-4 10 mg/m^2	Compound VII-4 10 mg/m^2	Unchanged
108	Unchanged	Unchanged	Compound VII-23 10 mg/m^2	Compound VII-23 10 mg/m^2	Unchanged
109	Dye I-2 0.2 g/m^2 III-3 0.3 g/m^2	Unchanged	Unchanged	Unchanged	Dye I-1 0.2 g/m^2
110	Dye I-4 0.2 g/m^2 III-2 0.3 g/m^2	Unchanged	Unchanged	Unchanged	Dye I-3 0.2 g/m^2
111	Dye I-6 0.2 g/m^2 III-12 0.3 g/m^2	Unchanged	Unchanged	Unchanged	Dye I-5 0.2 g/m^2

TABLE 1 Samples (cont'd)

	First Layer The Black Colloidal Silver	Second Layer In the Intermediate Layer	Fourth Layer In The Low Speed Red Sensitive Emulsion Layer	Ninth Layer In the Low Speed Green Sensitive Emulsion Layer	Thirteenth Layer The Black Colloidal Silver
112	Dye I-2 0.2 g/m^2 III-3 0.3 g/m^2	Compound VII-51	Unchanged	Unchanged	Dye I-1 0.2 g/m^2
113	Dye I-4 0.2 g/m^2 III-11 0.3 g/m^2	Compound VII-1	Unchanged	Unchanged	Dye I-3 0.2 g/m^2
114	Dye I-6 0.2 g/m^2 III-12 0.3 g/m^2	Unchanged	Compound VII-51 10 mg/m^2	Compound VII-51 10 mg/m^2	Dye II-5 0.3 g/m^2
115	Dye I-10 0.2 g/m^2 III-3 0.3 g/m^2	Unchanged	Compound VII-51 10 mg/m^2	Compound VII-1 10 mg/m^2	Dye II-6 0.3 g/m^2
116	Dye I-14 0.2 g/m^2 III-9 0.3 g/m^2	Unchanged	Compound VII-1 10 mg/m^2	Compound VII-1 10 mg/m^2	Dye III-1 0.2 g/m^2
117	Dye I-25 0.2 g/m^2 III-9 0.3 g/m^2	Unchanged	Compound VII-51 10 mg/m^2	Compound VII-1 10 mg/m^2	Dye III-13 0.2 g/m^2
118	Dye III-2 0.2 g/m^2 III-11 0.3 g/m^2	Unchanged	Compound VII-2 10 mg/m^2	Compound VII-2 10 mg/m^2	Dye IV-1 0.6 g/m^2
119	Dye III-4 0.2 g/m^2 III-11 0.3 g/m^2	Unchanged	Compound VII-4 10 mg/m^2	Compound VII-4 10 mg/m^2	Dye IV-2 0.2 g/m^2
120	Dye III-5 0.2 g/m^2 III-12 0.3 g/m^2	Unchanged	Compound VII-3 10 mg/m^2	Compound VII-3 10 mg/m^2	Dye IV-3 0.2 g/m^2
121	Dye III-6 0.2 g/m^2 III-12 0.3 g/m^2	Unchanged	Compound VII-5 10 mg/m^2	Compound VII-5 10 mg/m^2	Dye IV-4 0.2 g/m^2

TABLE 1 Samples (cont'd)

	First Layer The Black Colloidal Silver	Second Layer In the Intermediate Layer	Fourth Layer In The Low Speed Red Sensitive Emulsion Layer	Ninth Layer In the Low Speed Green Sensitive Emulsion Layer	Thirteenth Layer The Black Colloidal Silver
122	Dye III-8 0.2 g/m^2 III-16 0.3 g/m^2	Unchanged	Compound VII-22 10 mg/m^2	Compound VII-22 10 mg/m^2	Dye I-7 0.1 g/m^2 I-8 0.1 g/m^2
123	Dye IV-15 0.2 g/m^2 III-16 0.3 g/m^2	Unchanged	Compound VII-23 10 mg/m^2	Compound VII-23 10 mg/m^2	Dye I-9 0.2 g/m^2
124	Dye IV-15 0.2 g/m^2 III-3 0.3 g/m^2	Unchanged	Compound VII-26 10 mg/m^2	Compound VII-26 10 mg/m^2	Dye I-11 0.2 g/m^2
125	Dye V-1 0.2 g/m^2 III-11 0.4 g/m^2	Compound VII-51 10 mg/m^2	Unchanged	Compound VII-30 10 mg/m^2	Dye I-12 0.1 g/m^2
126	Dye V-1 0.2 g/m^2 III-19 0.4 g/m^2	Compound VII-51 10 mg/m^2	Unchanged	Compound VII-34 10 mg/m^2	Dye I-1 0.1 g/m^2 I-13 0.1 g/m^2
127	Dye V-1 0.2 g/m^2 III-3 0.4 g/m^2	Compound VII-1 10 mg/m^2	Unchanged	Compound VII-47 10 mg/m^2	Dye I-15 0.2 g/m^2
128	Dye V-2 0.2 g/m^2 III-9 0.4 g/m^2	Compound VII-48 10 mg/m^2	Unchanged	Compound VII-48 10 mg/m^2	Dye I-16 0.2 g/m^2
129	Dye V-3 0.2 g/m^2 III-9 0.4 g/m^2	Compound VII-49 10 mg/m^2	Unchanged	Compound VII-49 10 mg/m^2	Dye I-17 0.2 g/m^2
130	Dye V-4 0.4 g/m^2 III-16 0.4 g/m^2	Compound VII-50 10 mg/m^2	Unchanged	Compound VII-50 10 mg/m^2	Dye I-18 0.2 g/m^2

* In Samples 109 to 130, black colloidal silver is completely substituted with indicated dye mixture.

Method of Preparing Micro-crystalline Dispersions

The dye was dispersed in a vibrating ball mill using the method described below.

Water (21.7 ml), 3 ml of a 5% aqueous solution of p-octylphenoxyethoxyethane and 0.5 ml of a 5% aqueous solution of octylphenoxy-poly(degree of polymerization 10)oxyethylene ether were introduced into a 700 ml pot mill and 1.00 gram of the dye (I-1) of the present invention and 500 ml of zirconium oxide beads (diameter 1mm) were added and the contents were dispersed for 2 hours. The vibrating ball mill used was a BO model made by Chuo Kakoki.

The contents were removed from the ball mill, 8 grams of a 12.5% aqueous gelatin solution was added thereto, and the beads were removed by filtration to obtain a dye/gelatin dispersion.

Microcrystalline dispersions of the other dyes were obtained using the same method.

The samples 101 to 130 prepared in the way described above were evaluated with respect to 1. sharpness, 2. color reproduction and 3. de-silvering properties.

1. Sharpness

The samples thus prepared were subjected to a gray exposure through a step wedge for MTF measurement purposes with an exposure meter adjusted to a color temperature of 4800° K, and then developed and processed in the manner described above. Density measurements were made with a fine part densitometer using the positive images thus obtained, and the MTF value was calculated from this measurement. The results are shown in Table 2 as the values for the red sensitive layer and the green sensitive layer, for 10 cycle/mm.

2. Color Reproduction

Samples which had been subjected to a gray exposure through a continuous wedge at a radiation intensity of 20 cms with an exposure meter adjusted to a color temperature of 4800° K, samples which had been exposed through a red filter at a radiation intensity of 40 cms and samples which had been exposed at a radiation intensity of 160 cms through a green filter were developed and processed in the same manner as described in the sharpness test. The densities were measured and the speeds for the red sensitive layer and the green sensitive layer at a density of 0.5 were obtained.

The difference in the gray exposure speed and the red exposure speed of the red sensitive layer is given as a measure of red color reproduction. As the difference in speed becomes larger, the red appears brighter. In the same manner, the difference between the gray exposure speed and the green exposure speed of the green sensitive layer is given as a measure of green color reproduction.

Color purity was increased as the difference in speed became larger, to thereby provide brilliant colors.

The results obtained are shown in Table 2.

3. De-silvering Properties

Processing was carried out as described above, with the exception that the 1-thioglycerine content of the conditioner in the conditioning process of the development processing was reduced from 0.4 ml/liter to 0.04 ml/liter and with the bleaching time was shortened from 6 minutes to 4 minutes. The amount of silver remaining in the sample thus processed was measured.

The results obtained are shown in Table 2.

TABLE 2 Summary Table of Experimental Results

Sample	Sharpness		Color Reproduction $\Delta S_{0.5}$		De-Silvering Residual Silver ($\mu m/cm^2$)
	R	G	R	G	
Comparative Ex.					
101	1.05	1.10	0.25	0.20	5
102	1.15	1.12	0.32	0.22	10
103	1.16	1.12	0.33	0.23	11
104	1.15	1.22	0.35	0.33	15
105	1.17	1.23	0.34	0.32	14
106	1.16	1.22	0.33	0.33	16
107	1.15	1.21	0.33	0.32	15
108	1.16	1.23	0.34	0.33	14
109	1.04	1.06	0.24	0.15	2
110	1.02	1.07	0.23	0.16	1
111	1.02	1.07	0.23	0.17	1
This Invention					
112	1.15	1.22	0.36	0.33	3
113	1.15	1.23	0.35	0.33	2
114	1.16	1.24	0.33	0.32	2
115	1.17	1.22	0.34	0.31	1

TABLE 2 Summary Table of Experimental Results (cont'd)

Sample	Sharpness		Color Reproduction $\Delta S_{0.5}$		De-Silvering Residual Silver ($\mu m/cm^2$)
	R	G	R	G	
This Invention					
116	1.15	1.23	0.36	0.34	2
117	1.17	1.22	0.35	0.34	1
118	1.16	1.24	0.35	0.33	2
119	1.16	1.24	0.33	0.31	2
120	1.16	1.23	0.36	0.33	1
121	1.17	1.23	0.34	0.32	1
122	1.15	1.22	0.35	0.33	2
123	1.15	1.22	0.34	0.33	3
124	1.16	1.22	0.33	0.31	2
125	1.15	1.23	0.36	0.35	3
126	1.17	1.24	0.35	0.33	2
127	1.17	1.24	0.35	0.33	2
128	1.15	1.23	0.36	0.34	1
129	1.16	1.22	0.34	0.32	2
130	1.16	1.23	0.33	0.32	1

EXAMPLE 2

Preparation of Sample 201

The sample 201 was prepared by following the same procedure as Sample 116 except that the compound (1) of this invention was added at 0.10 g/m^2 in place of the dye added to Layer 13 (or the 13th layer in Sample 116 and also yellow colloidal silver was added to the layer at 0.05 g/m^2.

Preparation of Sample 202

The sample 202 was prepared by following the same procedure as Sample 119 except that the compound (1) of this invention was added at 0.10 g/m^2 in place of the dye added to Layer 13 in Sample 119 and also yellow colloidal silver was added to layer at 0.05 g/m^2.

Preparation of Sample 203

The sample 203 was prepared by following the same procedure as Sample 126 except that the compound (7) of this invention was added at 0.10 g/m^2 in place of the dye added to Layer 13 in Sample 126 and also yellow colloidal silver was added to layer at 0.05 g/m^2.

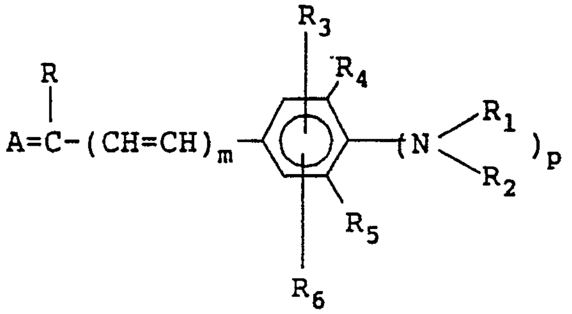
When, the samples 201 to 203 thus prepared were compared with the samples 116, 119, and 126, the same effects were obtained.

It is clearly seen from the results shown above that the present invention provides a silver halide color reversal sensitive material having greatly improved sharpness and color reproduction without reduction in de-silvering properties.

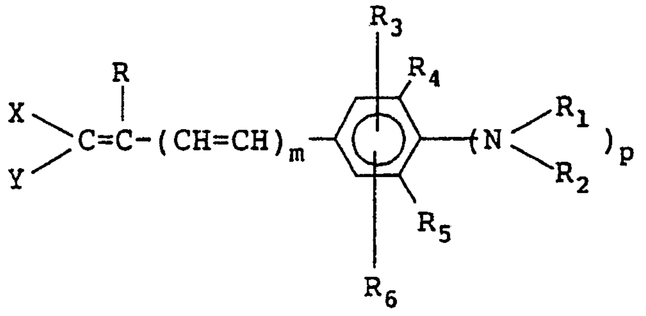
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver halide color reversal photographic photosensitive material comprising a support having thereon at least one red sensitive emulsion layer, at least one green sensitive emulsion layer and at least one blue sensitive emulsion layer, at least one hydrophilic colloid layer of said photographic photosensitive material containing a microcrystalline dispersion of at least one compound selected from the compounds represented by formulae (I), (II), (III), (IV), (V) and (VI), and at least one hydrophilic colloid layer of said photographic photosensitive material containing at least one compound represented by formula (VII).



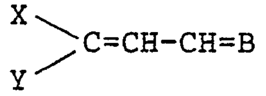
(I)



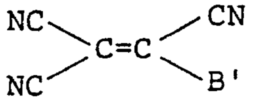
(II)

$$A=L_1-(L_2=L_3)_n-A' \qquad (III)$$

$$A=(L_1-L_2)_{2-q}=B \qquad (IV)$$



(V)



(VI)

wherein A and A′, which may be the same or different, each represents an acidic nucleus; B represents a basic nucleus; and X and Y, which may be the same or different, each represents an electron attractive group; R represents a hydrogen atom or an alkyl group; R_1 and R_2 each represent an alkyl group, an aryl group, an acyl group or a sulfonyl group, or R_1 and R_2 are joined together to form a five or six membered ring; R_3 and R_6 each represent a hydrogen atom, a hydroxy group, a carboxyl group, an alkyl group, an alkoxy group or a halogen atom; R_4 and R_5 each represent a hydrogen atom or a group of non-metal atoms joined together with R_1 and R_2, respectively, to form a five or six membered ring; L_1, L_2 and L_3 each represent a methine group; m represents 0 or 1, n and q each represent 0, 1 or 2, and p represents 0 or 1, and when p is 0, R_3 represents a hydroxy group or a carboxyl group and R_4 and R_5 each represent a hydrogen atom; B′ represents a heterocyclic group containing a carboxyl group, a sulfamoyl group or a sulfonamido group;

said compound represented by formulae (I) to (VI) containing at least one dissociable group such taht the pKa value of the compound in a 1 : 1 by volume mixed solvent comprising water and ethanol is within the range of from 4 to 11:

$A\text{-}(\mathrm{Time})_t\text{-}Z$ (VII)

wherein A represents a redox parent nucleus which eliminate $-(\mathrm{Time})_t\text{-}Z$ by oxidation during photographic development processing; Time represents a timing group which is bonded to A with a sulfur atom, a nitrogen atom, an oxygen atom or a selenium atom; t represents an integer of value 0 or 1; and Z represents a development inhibitor group.

2. A silver halide color reversal photographic photosensitive material as in claim 1, wherein the at least one dissociable group is a carboxyl group, a sulfamoyl group, a sulfonamido group or a hydroxy group.

3. A silver halide color reversal photographic photosensitive material as in claim 1, wherein the compound represented by formulae (I) to (VI) is substantially water insoluble at pH 6 or below pH 6, and is substantially water soluble at pH 8 or above pH 8.

4. A silver halide color reversal photographic photosensitive material as in claim 1, wherein the at least one compound represented by formulae (I) to (VI) is incorporated into a hydrophilic colloid layer of the photographic photosensitive material in an amount of from 1 to 1,000 mg/m^2.

5. A silver halide color reversal photographic photosensitive material as in claim 1, wherein the average particle diameter of the microcrystalline dispersion of the at least one compound selected from the formulae (I) to (VI) is not more than 10 μm.

6. A silver halide color reversal photographic photosensitive material as in claim 1, wherein a yellow filter layer and/or anti-halation layer of the photographic photosensitive material contains a compound represented by formulae (I) to (VI).

7. A silver halide color reversal photographic photosensitive material as in claim 1, wherein the compound represented by formula (VII) is contained in a silver halide emulsion layer in an amount of from 10^{-5} to 10^{-1} mol per mol of silver halide in the silver halide emulsion layer.