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

(11) Publication number: **0 326 161 A2**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **89101457.3**

(22) Date of filing: **27.01.89**

(51) Int. Cl.[4]: **G03C 7/26 , G03C 1/84**

(30) Priority: **28.01.88 JP 17771/88**

(43) Date of publication of application: **02.08.89 Bulletin 89/31**

(84) Designated Contracting States: **DE FR GB IT NL**

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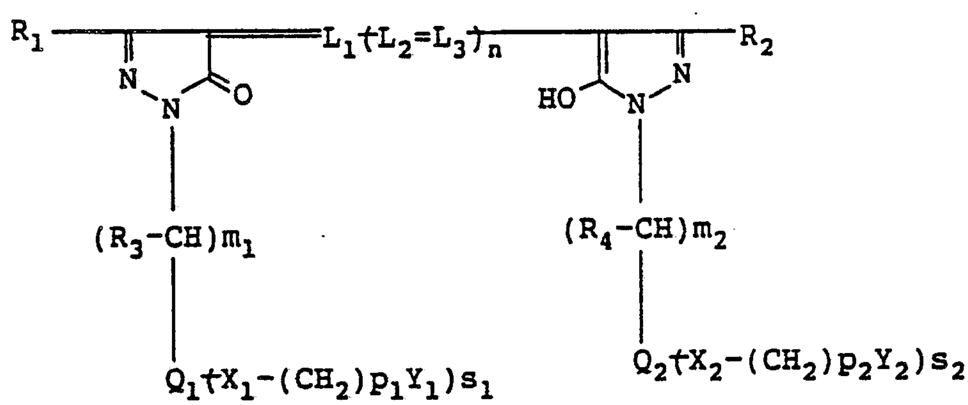
(54) **Silver halide color photographic materials.**

(57) A silver halide color photographic material which comprises a support having at least one silver halide color photographic emulsion layer coated thereon and containing at least one compound represented by the following general formula (I) and at least one compound represented by the following general formula (II) in at least one of hydrophilic layers provided on the support:



(I)

wherein each of R_1 and R_2 represents $-COOR_5$ or

$$-\mathrm{CON}\begin{matrix} R_5 \\ R_6 \end{matrix} ;$$

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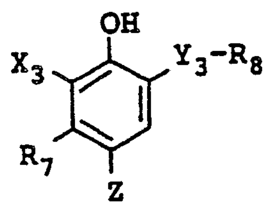
each of R_3 and R_4 represents hydrogen or an alkyl group; each of R_5 and R_6 represents a hydrogen atom, an unsubstituted alkyl group, an aryl group or R_5 and R_6 together form a 5- or 6-membered ring; each of Q_1 and Q_2 represents an aryl group; each of X_1 and X_2 represents a divalent bonding group or a bond; each of Y_1 and Y_2 represents a sulfonic acid group or a carboxylic acid group; each of L_1, L_2 and L_3 represents a methine group; each of m_1 and m_2 represents 1 or 2; n represents 0, 1 or 2; each of p_1 and p_2 represents 0, 1, 2, 3 or 4; and each of s_1 and s_2 represents 1 or 2; and



(II)

wherein Y_3 represents -NHCO- or -CONH-; R_8 represents an aliphatic group, an aromatic group, a heterocyclic group or an aryl amino group which may be substituted; X_3 represents hydrogen, a halogen atom, an alkoxy group or an acylamino group; R_7 represents a alkyl group (containing two or more carbon atoms), an acyl amino group or a nonmetallic atomic group necesasry to form a 5 to 7 membered ring by the combination of X_3 and R_7; and Z represents a hydrogen atom or a group which can be released by coupling with an oxidized color developing agent.

The materials give stable color images in long storage, high sharpness, high sensitivity and low fogging property because of using new dyes and couplers.

SILVER HALIDE COLOR PHOTOGRAPHIC MATERIALS

FIELD OF THE INVENTION

This invention relates to silver halide color photographic materials, particularly to silver halide color photographic materials for prints, and more particularly to silver halide photographic materials which give stable color images in long storage, sharp color image quality (which is called sharpness hereinafter), high photographic sensitivity and low photographic fog.

BACKGROUND OF THE INVENTION

Silver halide color photographic materials are usually spectrally sensitized by adding spectral sensitizers to silver halides according to the subtractive primary colors. A yellow dye-forming coupler, a magenta dye-forming coupler and a cyan dye-forming coupler are contained in the blue-sensitive silver halide emulsion layer, the green-sensitive silver halide emulsion layer and the red-sensitive silver halide emulsion layer, respectively. After conducting imagewise exposure, the silver halide color photographic materials are then processed with a color developing solution comprising an aromatic primary amine color developing agent and then with a bleach-fix bath to obtain an image.

The resulting color image, however, is not always stable to light, heat or moisture. Particularly, the cyan dye image has a larger dark discoloration caused by heat or moisture than both the yellow dye image and the magenta dye image, which changes the color balance. This is a great problem in practical use (for example, the print is turned reddish-brown when preserved in an album).

In order to solve the above problem, JP-A-56-80045 (British Patent 2,066,494; the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-56-104333 (British Patent 2,068,943), JP-B-57-37857 (U.S. Patent 4,333,999) (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-A-58-105229 (U.S. Patent 4,430,423), and JP-A-60-24547 (U.S. Patent 4,565,777) teach that couplers substituted at the 2 and 5 positions of the benzene ring of phenol with acyl amino groups, i.e., "2,5-diacylaminophenolic" couplers, are especially excellent as couplers to form very fast cyan-dye images. Also, phenolic cyan couplers having a C_2 or higher alkyl group in the 5-position of phenol can form very fast cyan-dye images.

These phenolic cyan couplers are quite useful for producing color photographic images which are very fast against heat and are preserved well. In addition, it is known that the photographic materials using these couplers are stable in processing and excellent in reproducing colors, particularly because of preservation of cyan density in bleach-fix processing.

Thus the above-mentioned phenolic couplers are favorable compounds to be used as the cyan-dye-forming couplers in color photographic materials.

The standard conditions for selecting the cyan couplers include, for example, light resistance, spectral absorption characteristics of dyes, and effect on photographic properties. Cyan couplers which satisfy all these properties are desired.

On the other hand, another important property needed for color photographic materials for prints is image quality, which is exceedingly influenced by sharpness.

In order to improve the sharpness of color images, the following two techniques are usually used. One is to prevent unsharpening of an image caused by the halation caused by reflecting the light scattered during or after transmission through silver halide emulsion layers on the interface between a silver halide emulsion and a base or on the surface of a photographic material opposite to silver halide emulsion layers and inducing again the reflecting light into the silver halide emulsion layers; and the other is to prevent unsharpening of an image caused by the irradiation caused by the scattering of light on the surface of silver halide in the silver halide emulsion layers.

Silver halide color photographic materials for prints usually employ the method of preventing irradiation.

In order to prevent irradiation, silver halide emulsion layers are colored. Usually, these layers to be colored consist of hydrophilic colloids, therefore, water-soluble dyes are usually contained in the layers for coloring. The dyes should satisfy the following conditions.

(1) The dyes must have the correct spectral absorption fit for the purpose of use thereof.

2) The dyes must be photochemically inert, i.e., exert no chemical effect on the properties of silver halide photographic emulsion layers, for example, lowering of sensitivity, fading of the latent image and causing photographic fog.

3) The dyes must be decolored in photographic processing or dissolved and removed to give no undesired color on the processed photographic materials.

In order to find the dyes which satisfy the above conditions, those skilled in the art have eagerly studied and the following dyes have been found, namely, oxonol dyes having pyrazolone or barbituric acid nuclei described in British Patents 506,385; 1,177,429; 1,311,884; 1,338,799; 1,385,371; 1,467,214; 1,433,102; and 1,553,516; JP-A-48-85103 (British Patent 1,373,026); JP-A-49-114420 (British Patent 1,433,102); JP-A-55-161233; JP-A-59-111640; U.S. Patents 3,247,127; 3,469,985; and 4,078,933; the other oxonol dyes described in U.S. Patents 2,533,472 and 3,379,533; and British Patent 1,278,621; azo dyes described in British Patents 575,691; 680,631; 599,623; 786,907; 907,125; and 1,045,609; U.S. Patent 4,255,326; and JP-A-59-211043; azomethine dyes described in JP-A-50-100116; JP-A-54-118247; British Patents 2,014,598 and 750,031; anthraquinone dyes described in U.S. Patent 2,865,752; allylidene dyes described in U.S. Patents 2,538,009; 2,688,541; and 2,538,008; British Patents 584,609 and 1,210,252; JP-A-50-40625; JP-A-51-3623; JP-A-51-10927; JP-A-54-118247; JP-B-48-3286 and JP-A-59-37303; styryl dyes described in JP-B-28-3082, JP-B-44-16594, and JP-B- 59-28898; triarylmethane dyes described in British Patents 446,583 and 1,335,422; and JP-B-59-228250; merocyanine dyes described in British Patents 1,075,653; 1,153,341; 1,284,730; 1,475,282; and 1,542,807; and cyanine dyes described in U.S. Patents 2,843,486 and 3,294,539.

Of these dyes, the oxonol dyes having two pyrazolone nuclei have been used for coloring photographic materials as useful dyes which are decolored in a developing solution containing sulfite and exert little harmful influence on photographic emulsions.

However, many of the oxonol dyes having two pyrazolone nuclei have defects of spectrally sensitizing the undesired areas of silver halide emulsions themselves or of the spectrally sensitized silver halide emulsions, causing a decrease of sensitivity, probably because of dropping off spectral sensitizers, and increasing fog.

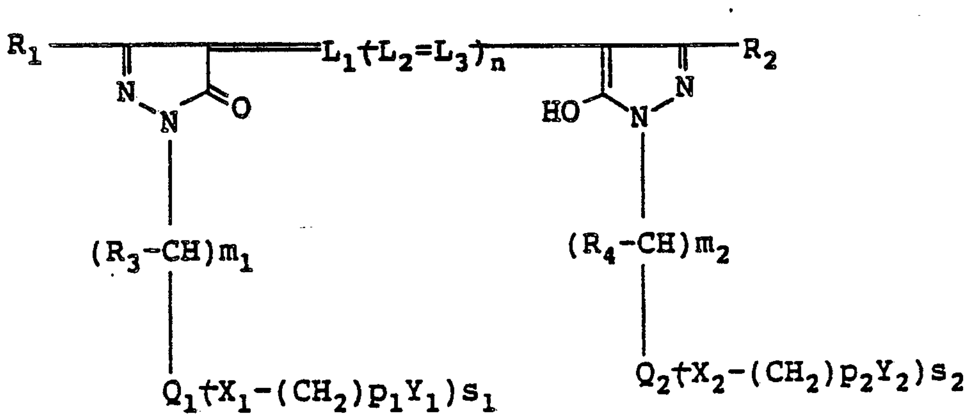
Moreover, some of them leave after development processing which is conducted more rapidly recently. In order to overcome the problem, it has been proposed to use dyes having high reactivity with sulfite ions, but these dyes have defects that they are not sufficiently stable in dry films to cause the decrease of density after the lapse of time and give no desired photographic effect.

In addition, combinations of the above dyes and thermally fast couplers, for example, the above-mentioned 2,5-diacylaminophenolic couplers, cause the lowering of sensitivity and the increase of fog. This is a great problem in practical use. JP-A-60-225155 discloses that photographic materials prepared by combining 2,5-diacylaminophenolic couplers and specific oxonol dyes have high resistance to dark discoloration, excellent sharpness, good latent image stability and high whiteness (low fog), but it has been found that the above combinations are not satisfactory in respect of sharpness and fog.

SUMMARY OF THE INVENTION

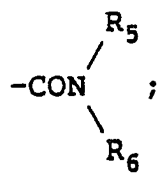
An object of the present invention is to provide silver halide color photographic materials including light-sensitive silver halide which give stable color images in long storage, high sharpness, high photographic sensitivity and low photographic fog by means of new water-soluble dyes which are easily decolored by processing and stable in storage without exerting any harmful influence on the photographic characteristics of the silver halide emulsion layers.

The objects of the present invention can be attained by a silver halide color photographic material comprising a support having at least one silver halide color photographic emulsion layer coated thereon and containing at least one compound represented by the following general formula (I) and at least one compound represented by the following general formula (II) in at least one of hydrophilic colloid layers provided on the support:

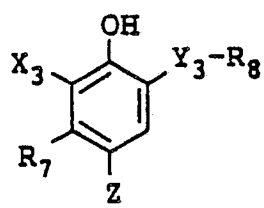


(I)

wherein each of R_1 and R_2 represents $-COOR_5$ or



each of R_3 and R_4 represents hydrogen or an alkyl group; each of R_5 and R_6 represents hydrogen, an alkyl group, an aryl group, or R_5 and R_6 together form a 5- or 6-membered ring; each of Q_1 and Q_2 represents an aryl group (2- or 3-valent); each of X_1 and X_2 represents a divalent bonding group or a bond; each of Y_1 and Y_2 represents a sulfonic acid group or a carboxylic acid group; each of L_1, L_2 and L_3 represents a methine group; each of m_1 and m_2 represents 1 or 2; n represents 0, 1 or 2; each of p_1 and p_2 represents 0, 1, 2, 3 or 4; and each of s_1 and s_2 represents 1 or 2;



(II)

wherein Y_3 represents -NHCO- or -CONH-; R_8 represents an aliphatic group, an aromatic group, a heterocyclic group or a substituted or unsubstituted aryl amino group; X_3 represents hydrogen, a halogen atom, an alkoxy group or an acylamino group; R_7 represents an alkyl group (containing two or more carbon atoms) or an acyl amino group, or a nonmetalic atomic group necessary to form a 5 to 7 membered ring by the combination of R_7 with X_3; and Z represents a hydrogen atom or a group which can be released by coupling with an oxidized developing agent.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention terms "alkyl group (or alkyl moiety)", "aryl group (or aryl moiety)", and "aromatic group" each represents substituted and unsubstituted.

The following is a detailed explanation of dyes represented by formula (I).

In formula (I), each of R_1 and R_2 represents $-COOR_5$ or

$$-CON\begin{matrix} R_5 \\ \diagup \\ \\ \diagdown \\ R_6 \end{matrix} ;$$

each of R_3 and R_4 represents hydrogen or an alkyl group (e.g., methyl, ethyl); each of R_5 and R_6 represents hydrogen, an unsubstituted alkyl group (e.g., methyl, ethyl, isopropyl, butyl); a substituted alkyl group [examples of the substituents include a sulfo group (e.g., sufomethyl, sulfoethyl), a carboxyl group (e.g., carboxymethyl, carboxyethyl), a hydroxy group (e.g., hydroxyethyl, 1,2-dihydroxypropyl), an alkoxy group (e.g., methoxyethyl, ethoxyethyl), a halogen atom [e.g., fluorine, chlorine, bromine (e.g., 2-chloroethyl, 2-bromoethyl, 2,2,2-trifluoroethyl)], a cyano group (e.g., cyanoethyl), an aliphatic or aromatic-sulfonyl group (e.g., methanesulfonylethyl), a nitro group (e.g., 2-nitrobutyl, 2-nitro-2-methylpropyl), an amino group unsubstituted or substituted with an alkyl group such as a methyl group and an ethyl group (e.g., dimethylaminoethyl, diethylaminopropyl), an aryl group (e.g., benzyl, p-chlorobenzyl)]; a phenyl -group, and a substituted phenyl group [examples of the substituents include a sulfo group (e.g., p-sulfophenyl, o,p-disulfophenyl), a carboxyl group (e.g., p-carboxyphenyl, m-carboxyphenyl), a hydroxy group (e.g., p-hydroxyphenyl, m-hydroxyphenyl), an alkoxy group (e.g., p-methoxyphenyl, m-ethoxyphenyl), a halogen atom (e.g., p-chlorophenyl, p-bromophenyl, p-fluorophenyl), a cyano group (e.g., p-cyanophenyl, o-cyanophenyl), a nitro group (e.g., p-nitrophenyl, m-nitrophenyl), an amino group unsubstituted or substituted with an alkyl group such as a methyl group and an ethyl group (e.g., p-dimethylaminophenyl, p-diethylaminophenyl), or an alkyl group (e.g., p-methylphenyl, o-methylphenyl)]. When R_1 and R_2 represent $-COOR_5$ and R_5 represents hydrogen, R_1 and R_2 represent carboxyl groups, which may form not only a free acid but a salt (e.g., sodium salt, potassium salt, ammonium salt, tetraammonium salt).

Also, R_5 and R_6 may form a 5 to 6 membered ring (e.g., morpholino, piperidino). Each of Q_1 and Q_2 represents a 2- or 3-valent unsubstituted aryl group (e.g., phenyl, naphthyl), a 2- or 3-valent substituted phenyl group [examples of the substituents include a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group, a halogen atom (chlorine, bromine, fluorine), an aliphatic or aromatic carbamoyl group (e.g., ethylcarbamoyl), an aliphatic or aromatic sulfamoyl group (e.g., ethylsulfamoyl), a cyano group, a nitro group, an alkylsulfonyl group (e.g., methanesulfonyl), an arylsulfonyl group (e.g., benzenesulfonyl), an amino group unsubstituted or substituted with an alkyl group such as a methyl group and an ethyl group (e.g., dimethylamino), an aliphatic or aromatic acylamino group (e.g., acetylamino), and an aliphatic or aromatic sulfonamido group (e.g., methanesulfonamido)]. Q_1 and Q_2 may be bonded with the other moieties at any positions. Each of X_1 and X_2 represents a divalent bonding group and more particularly,

$$-O-,\ \begin{matrix} R_7 \\ | \\ -N- \end{matrix},\ \begin{matrix} R_7 \\ | \\ -N-CO- \end{matrix},$$

$$-SO_2,\ \begin{matrix} R_7 \\ | \\ -N-SO_2 \end{matrix},$$

or a bond, wherein R_7 represents hydrogen, a C_1 to C_5 alkyl group, or a C_1 to C_5 (total) substituted alkyl group [examples of the substituents include a C_1 to C_3 alkoxy group, a sulfo group (e.g., sulfoethyl, sulfopropyl), a carboxyl group (e.g., carboxylethyl), a cyano group, a hydroxy group (e.g., hydroxyethyl), an amino group unsubstituted or substituted with an alkyl group such as a methyl group and an ethyl group, an aliphatic or aromatic sulfonamido group (e.g., methane sulfonamido), an aliphatic or aromatic carbonamido group (e.g., acetylamino), an aliphatic or aromatic carbamoyl group (e.g., ethylamino carbonyl), and an aliphatic or aromatic sulfamoyl group (e.g., ethylaminosulfonyl)]. Each of Y_1 and Y_2 represents a sulfonic acid group or a carboxylic acid group, which may form not only a free acid but a salt (e.g., sodium salt, potassium salt, ammonium salt, tetraammonium salt). Each of L_1, L_2 and L_3 represents a methine group, or a substituted methine group (where the substituents include a methyl group, an ethyl group and a phenyl group). Each of m_1 and m_2 represents 1 or 2; n represents 0, 1, or 2; each of p and p_2 represents 0, 1, 2, 3 or 4; each of s_1 and s_2 represents 1 or 2.

In the compounds represented by formula (I), each of R_3 and R_4 is preferably hydrogen or a methyl group; each of R_5 and R_6 is preferably hydrogen, a C_1 to C_4 alkyl group, a C_1 to C_6 substituted alkyl group [examples of the substituents preferably include a sulfo group, a carboxyl group, a hydroxy group, a C_1 to C_2 alkoxy group, a chlorine atom, a cyano group, an amino group, and a C_1 to C_4 alkylamino group], a phenyl group or a substituted phenyl group [examples of the substituents preferably include a sulfo group, a carboxyl group, a C_1 to C_4 alkoxy group, a chlorine atom, a cyano group, a C_1 to C_4 alkyl group, an amino group, and a C_1 to C_4 alkyl group, an amino group, and a C_1 to C_4 alkylamino group]. Also, R_5 and R_6 preferably form a 5-membered ring or a 6-membered ring (e.g., a morpholino ring, a pyrolidine ring, a piperidine ring). Each of Q_1 and Q_2 preferably is a phenylene group, a substituted phenylene group [where the substituents preferably include a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group, a halogen atom (e.g., chlorine, bromine, fluorine) and a C_1 to C_4 dialkylamino group].

When each of n, m_1, m_2, P_1, P_2, S_1, and S_2 is plural, each set of groups may be the same or different.

Each of X_1 and X_2 preferably represents

$$-O-,\quad -\overset{\displaystyle R_7}{\overset{|}{N}}-$$

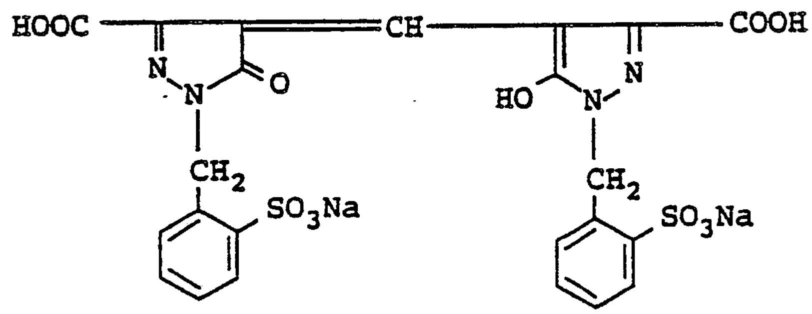
or a bond wherein R_7 preferably represents hydrogen, a C_1 to C_5 alkyl group, or a C_1 to C_5 substituted alkyl group [examples of the substituents include a C_1 to C_3 alkoxy group, a cyano group, a hydroxy group and a C_1 to C_4 alkylamino group].

Moreover, of the dyes prepresented by formula (I), the most preferred dye is obtained when $m_1 = m_2 = 1$.

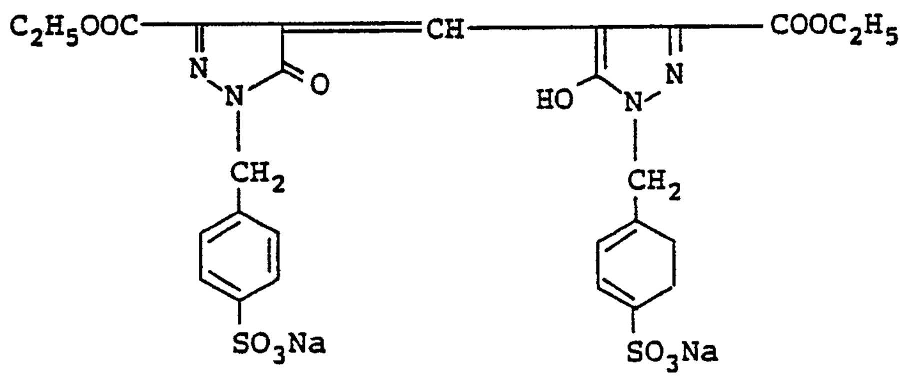
Since the dyes of the present invention are preferably those which are able to dissolve into a processing solution easily thereby come out from the photographic material, the carbon numbers of an alkyl group and an aryl group preferably are small.

The following are examples of compounds represented by formula (I), which shall not restrict the scope of the present invention.

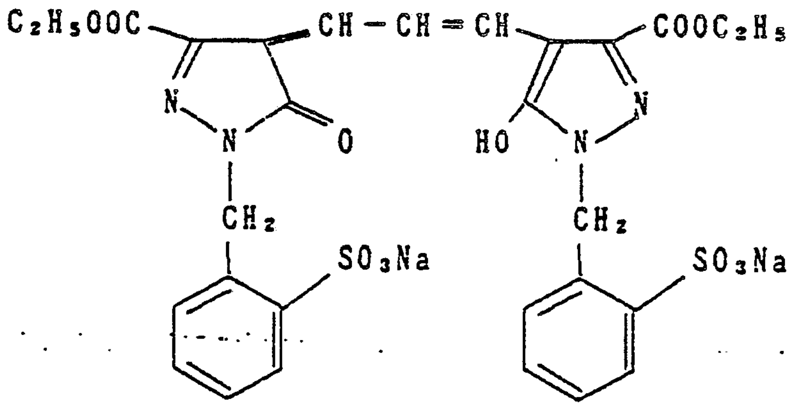
I-1



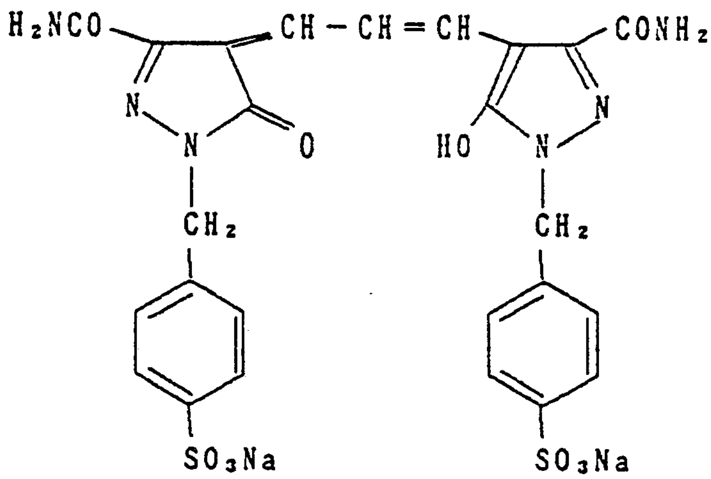
I-2



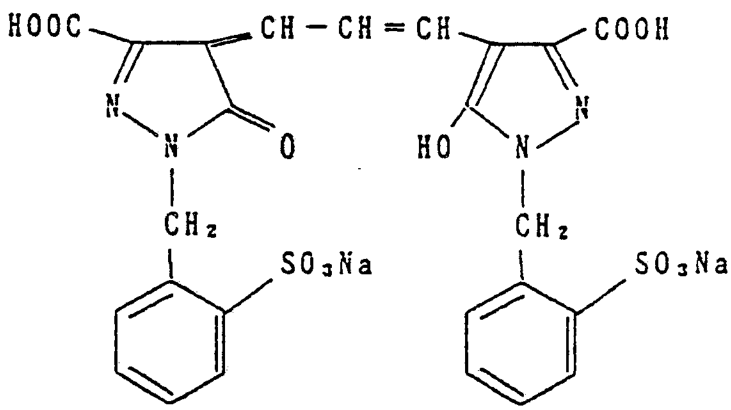
I − 3



I − 4



I − 5



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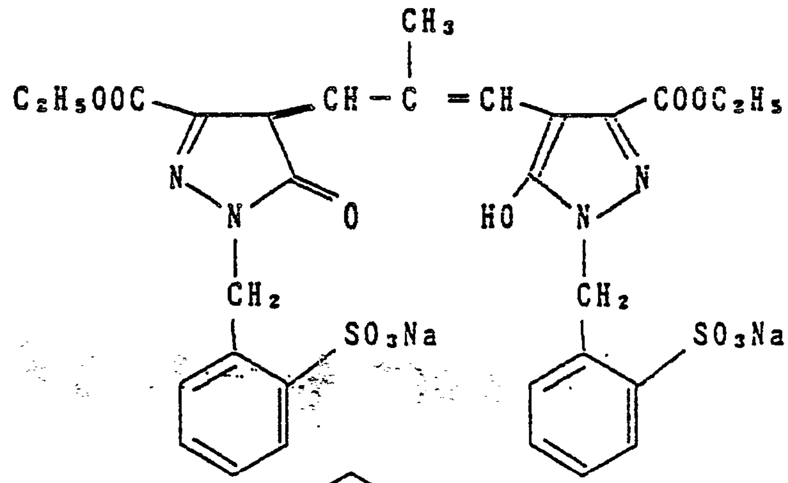

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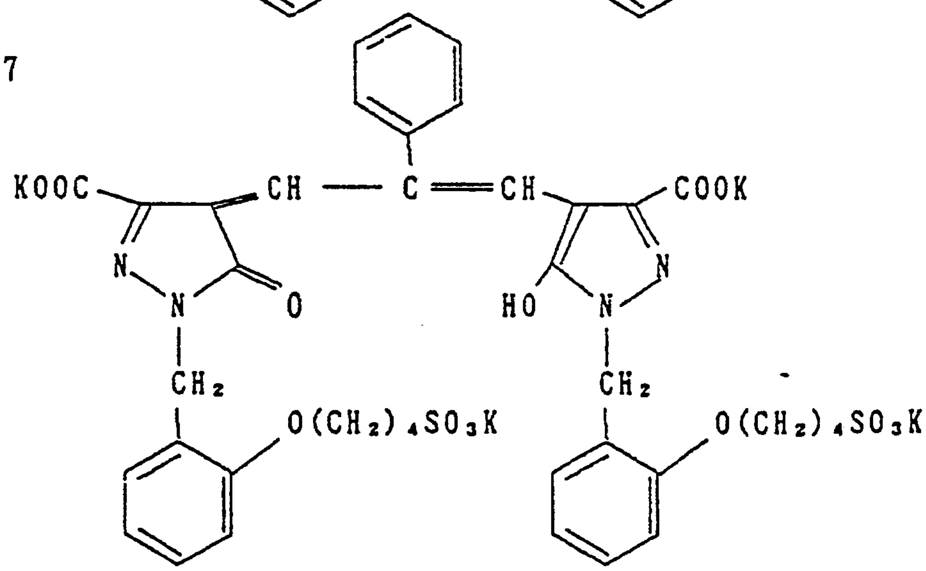

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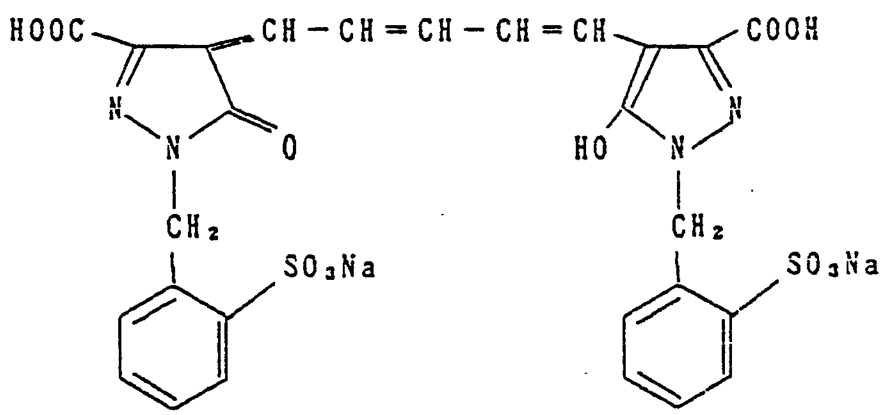
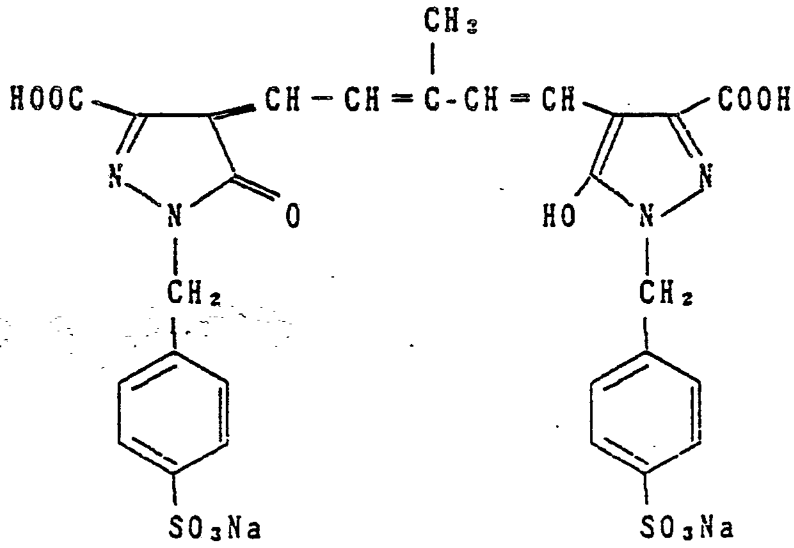
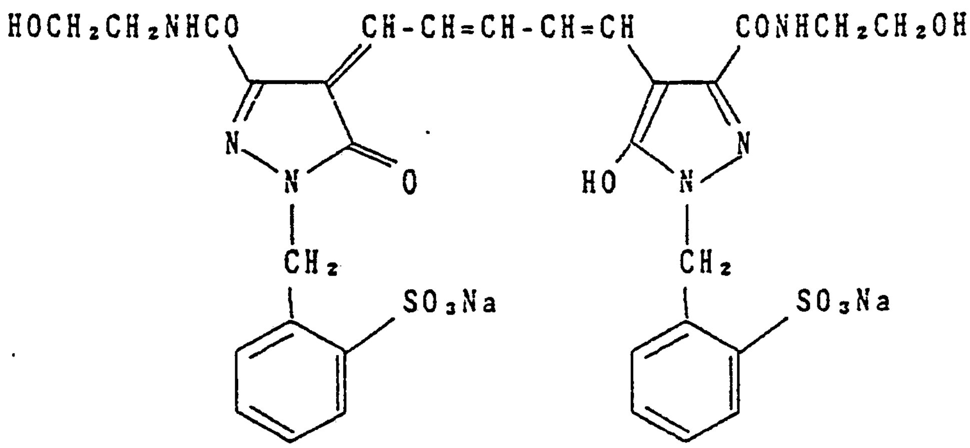


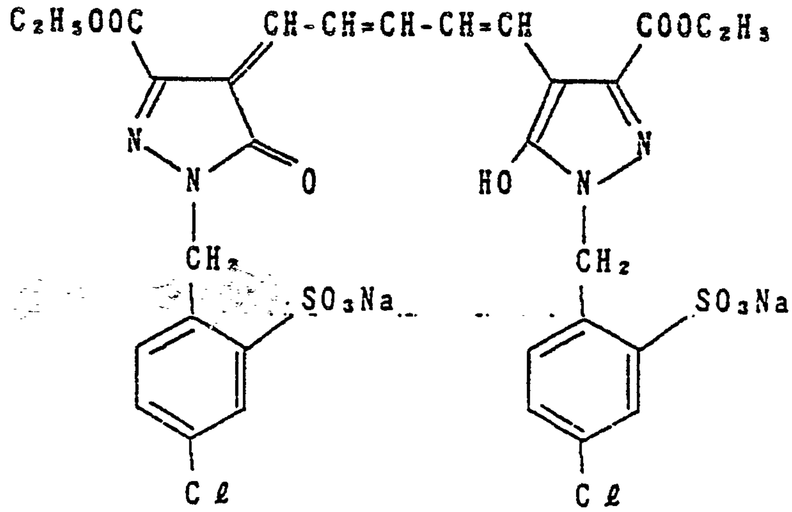
I - 9



I - 1 0



I－11



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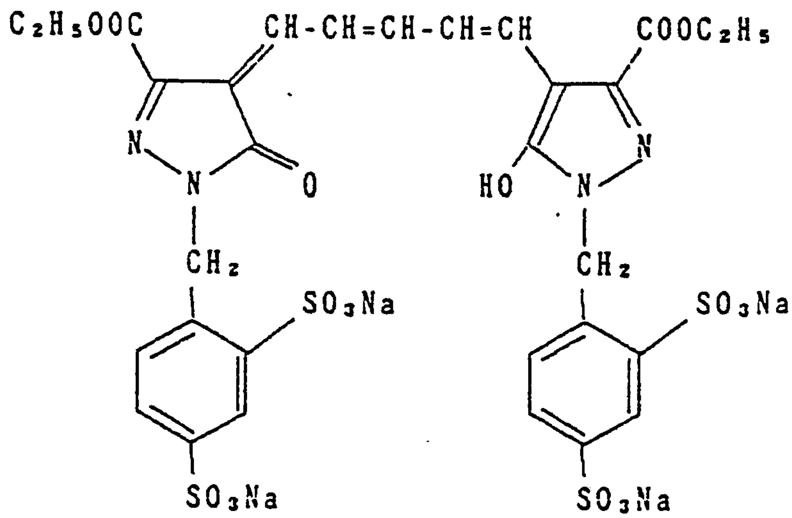
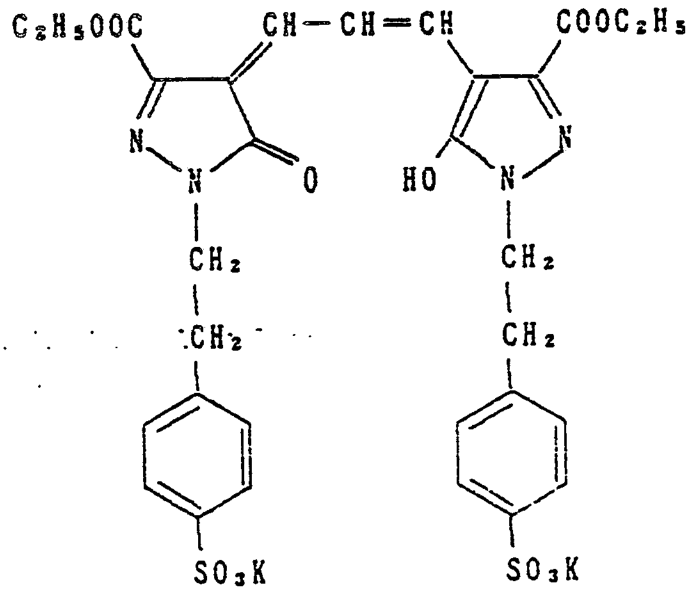


I－13



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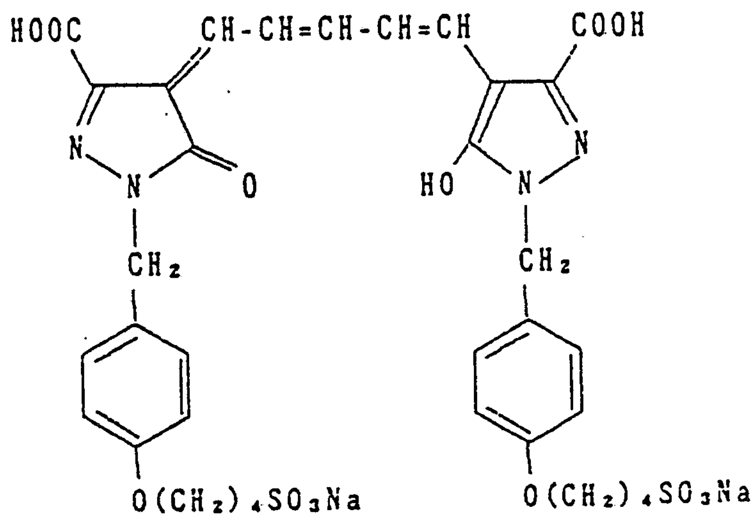

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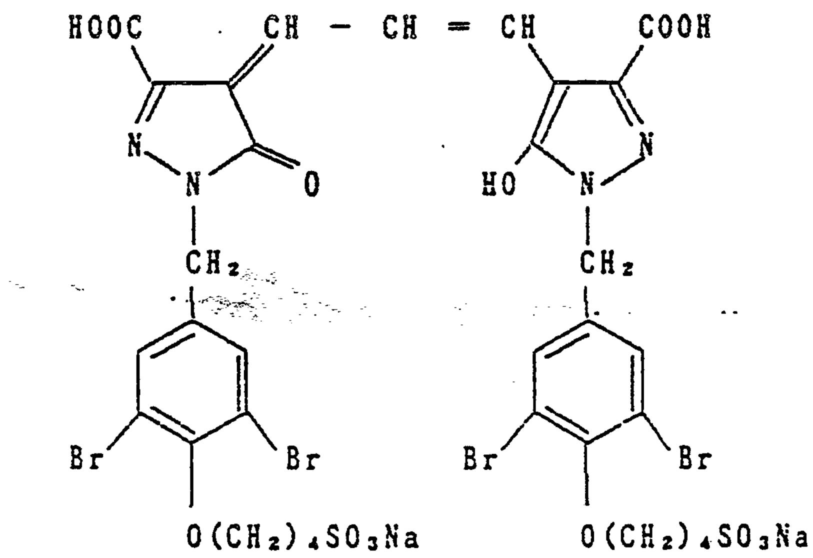
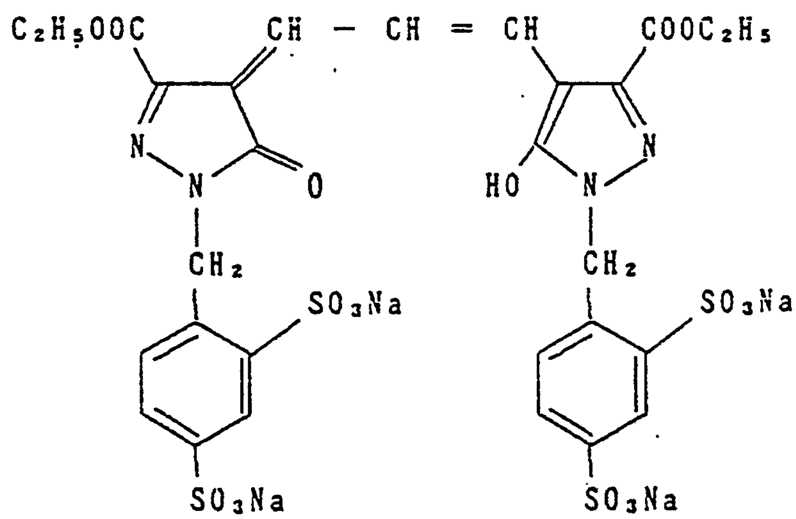
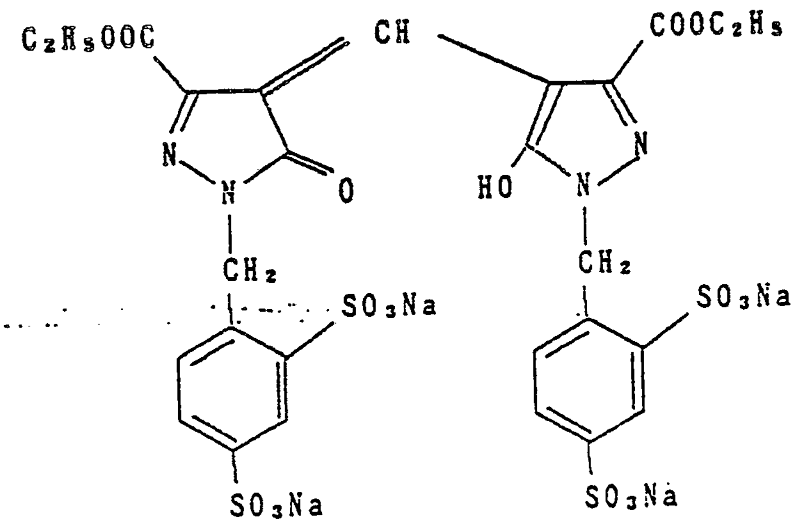


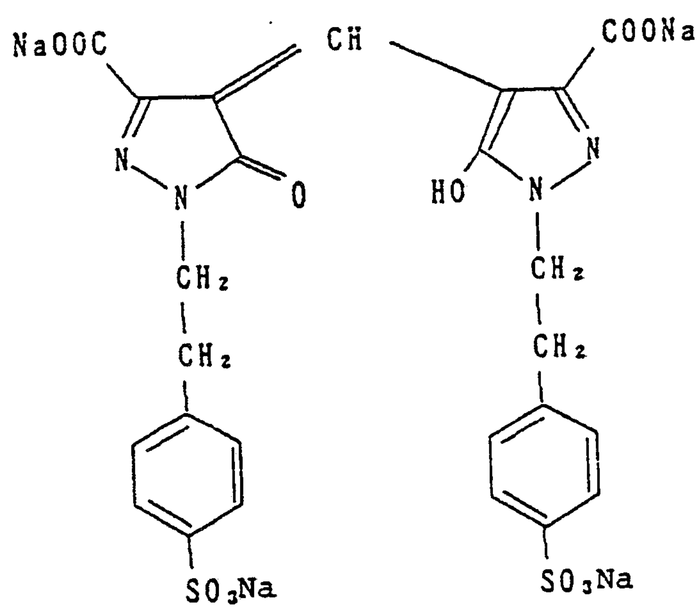
I－16



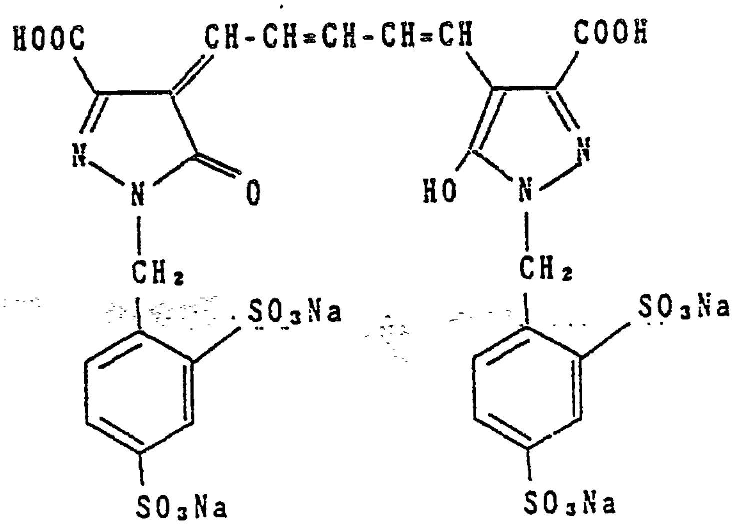
I - 1 7



I - 1 8



I − 1 9



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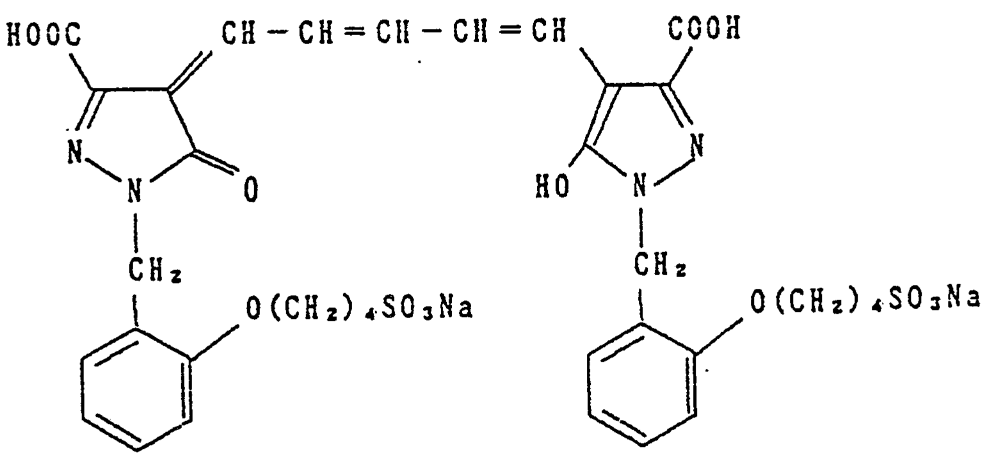
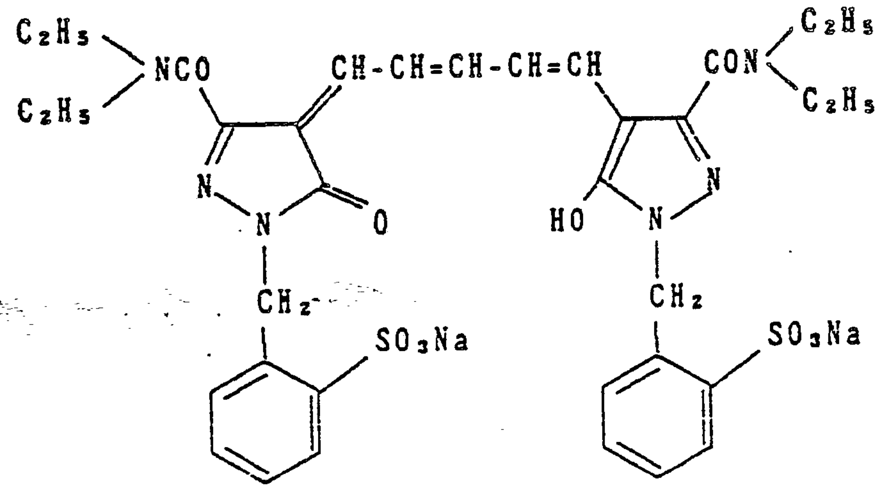


I - 2 1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C2H5
CH-CH=CH-CH=CH
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C2H5
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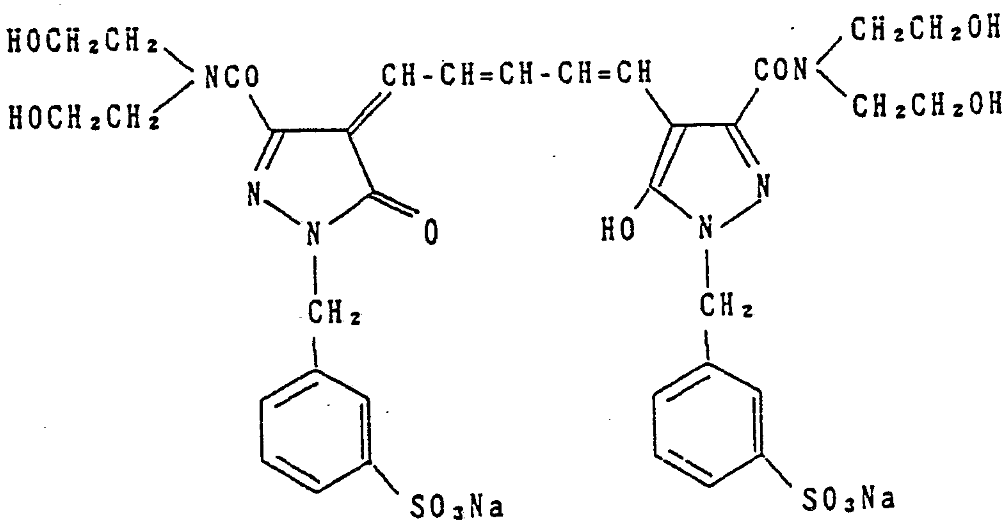
N
O
HO
N
N
CH2
CH2
SO3Na
SO3Na

I - 2 2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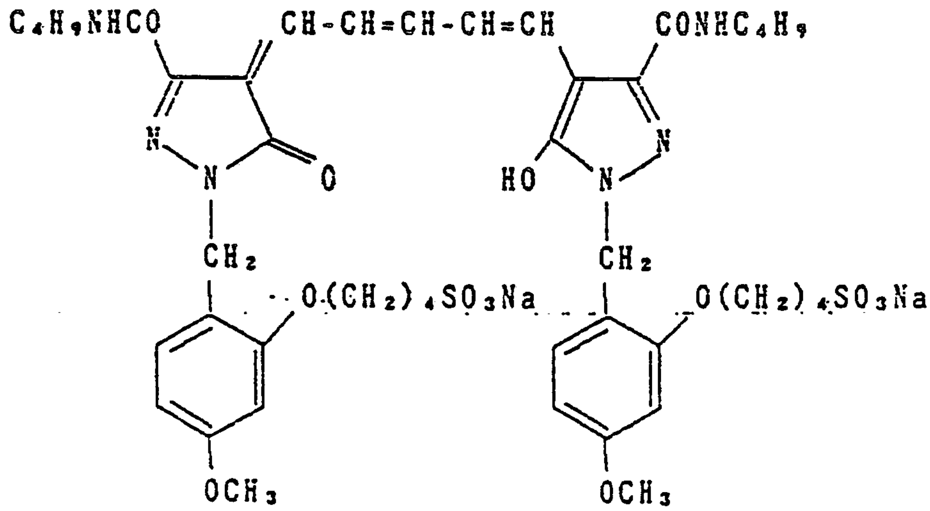
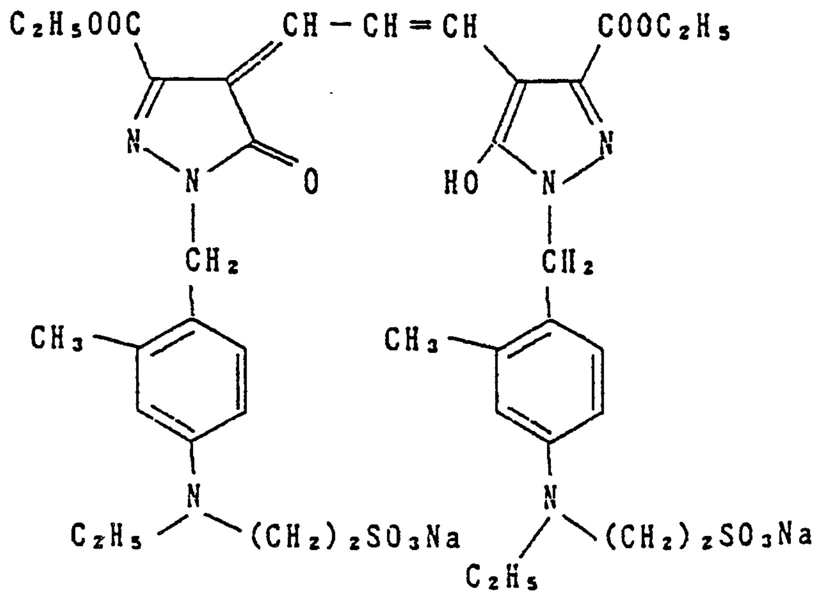
SO3Na
SO3Na

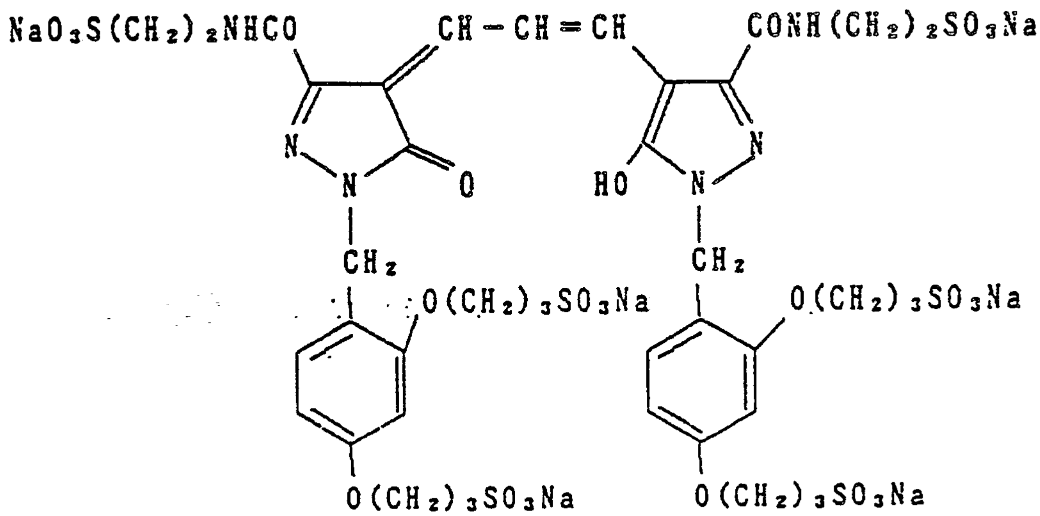
I - 2 3



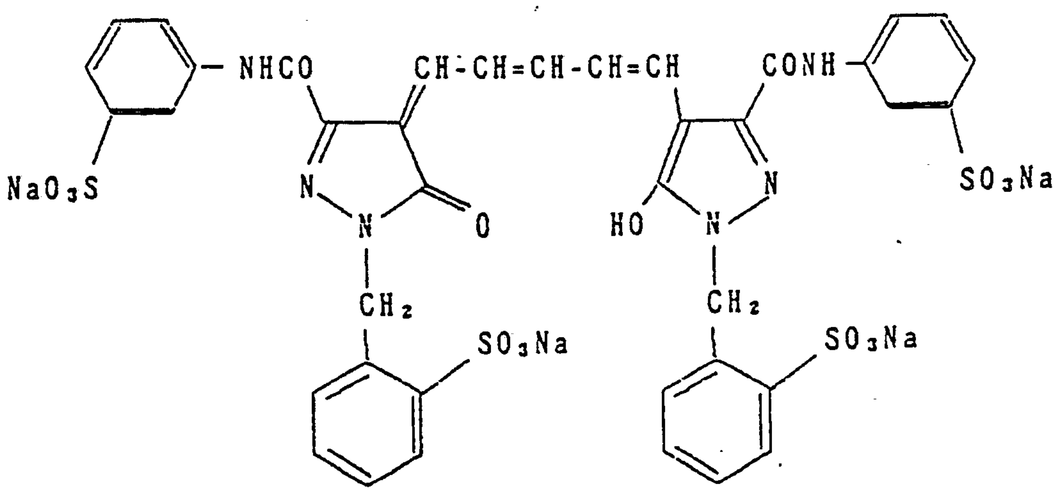
I - 2 4



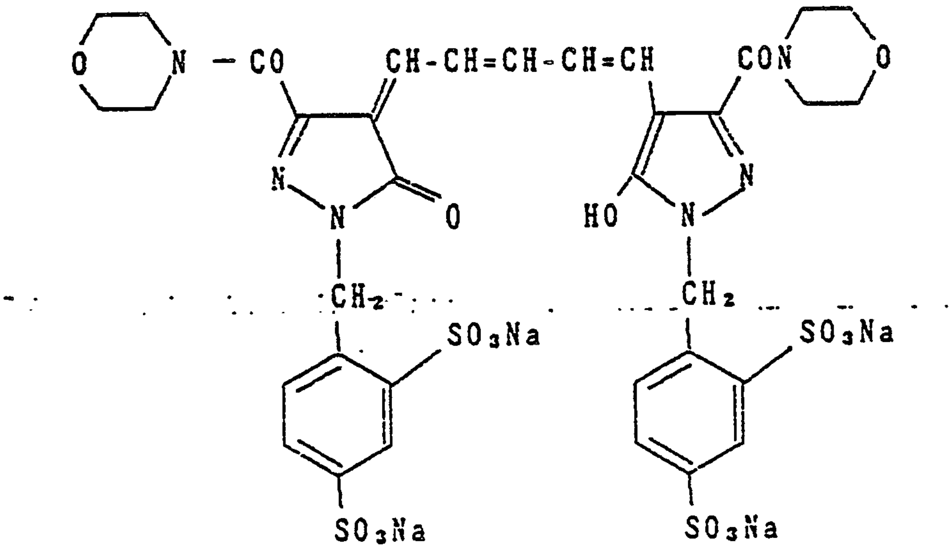
I - 2 5



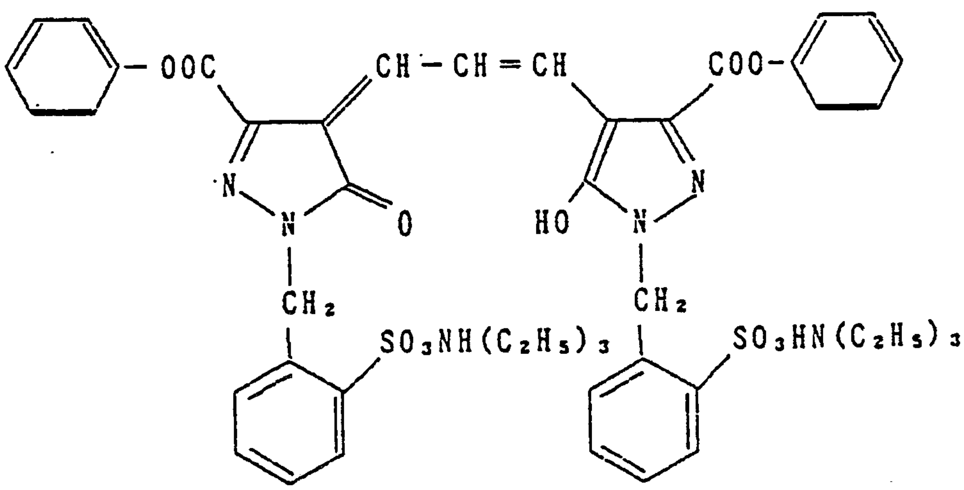
I - 2 6



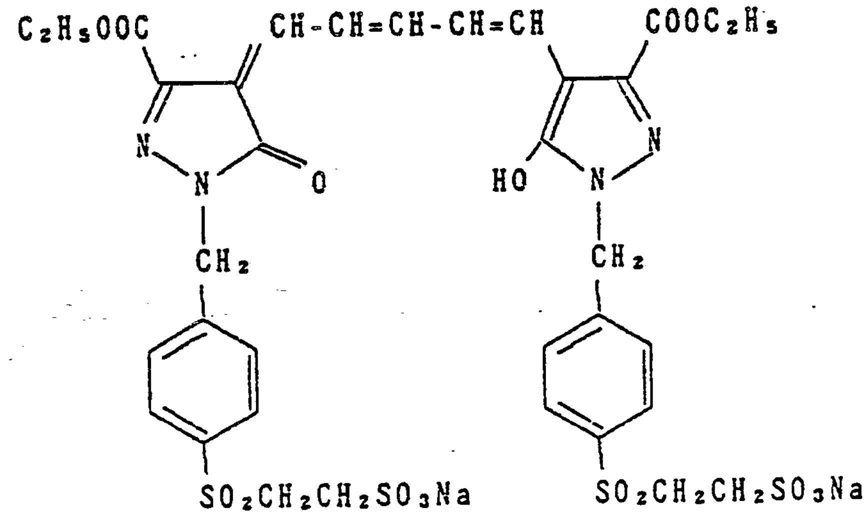
I - 2 7



I - 2 8



I－２９



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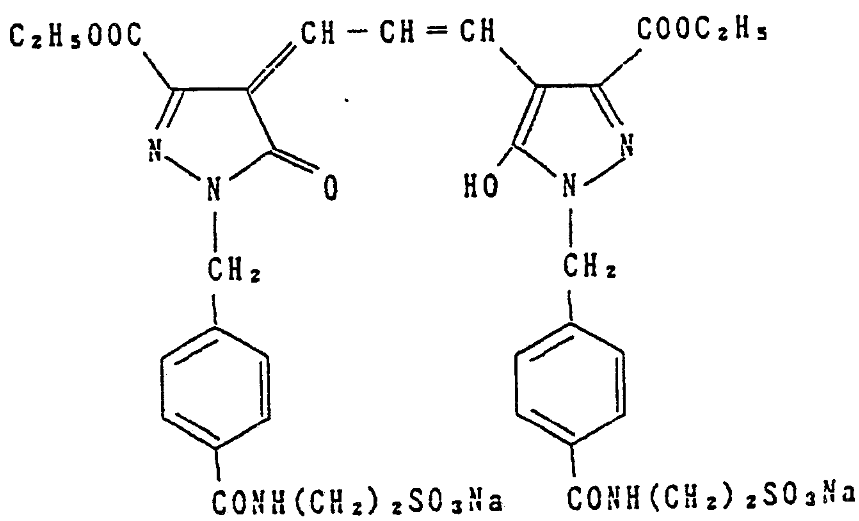

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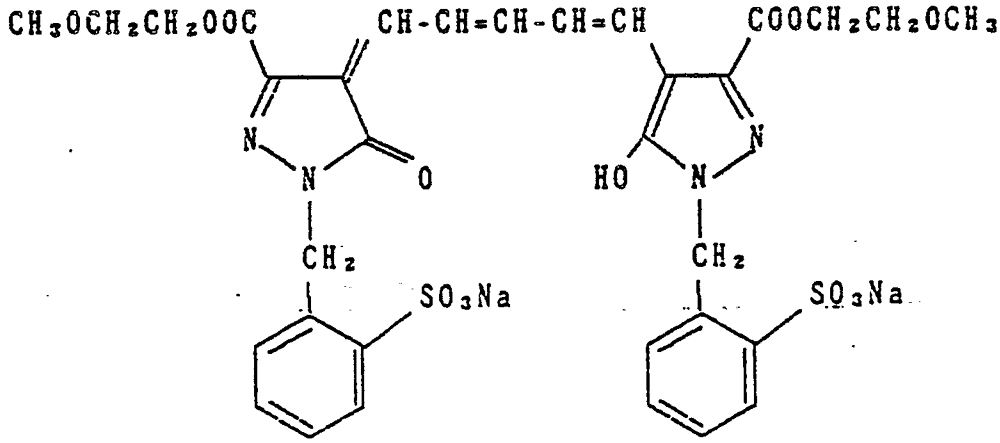

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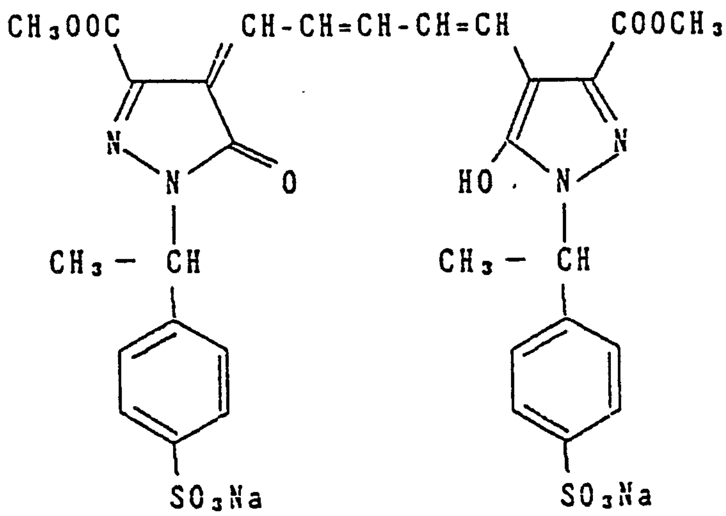
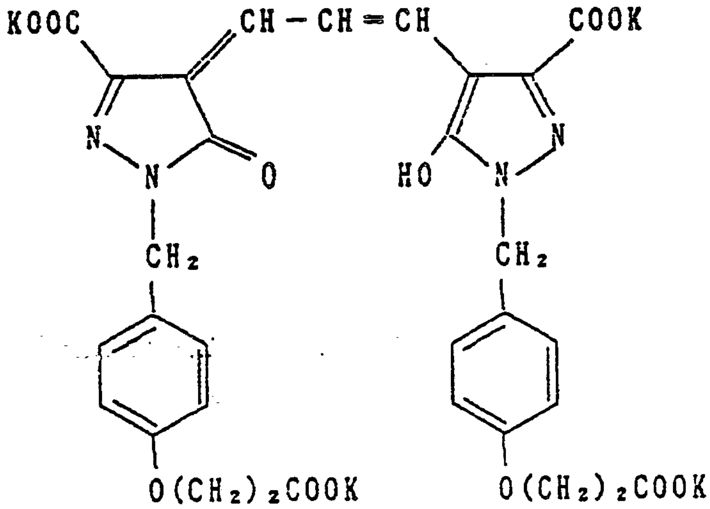


I - 3 3



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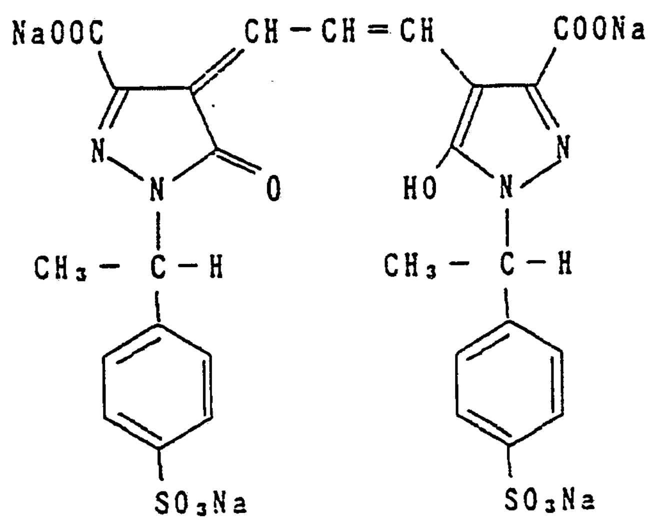
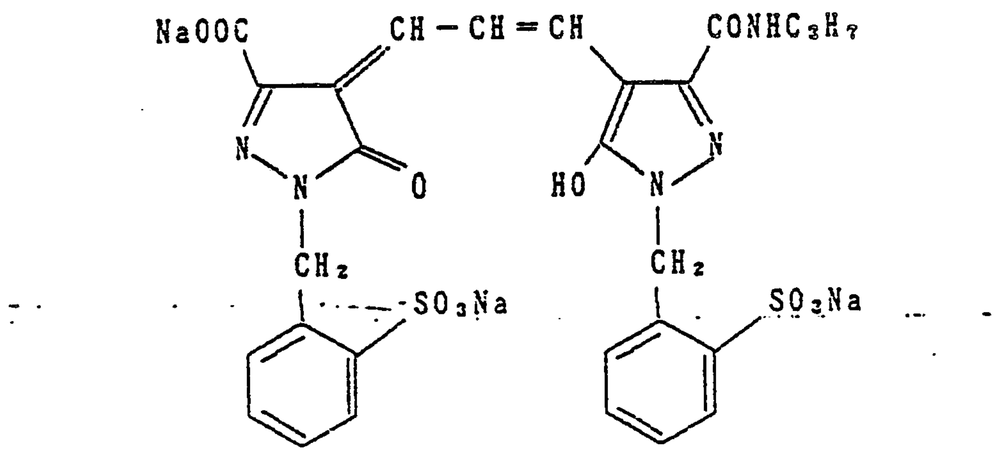
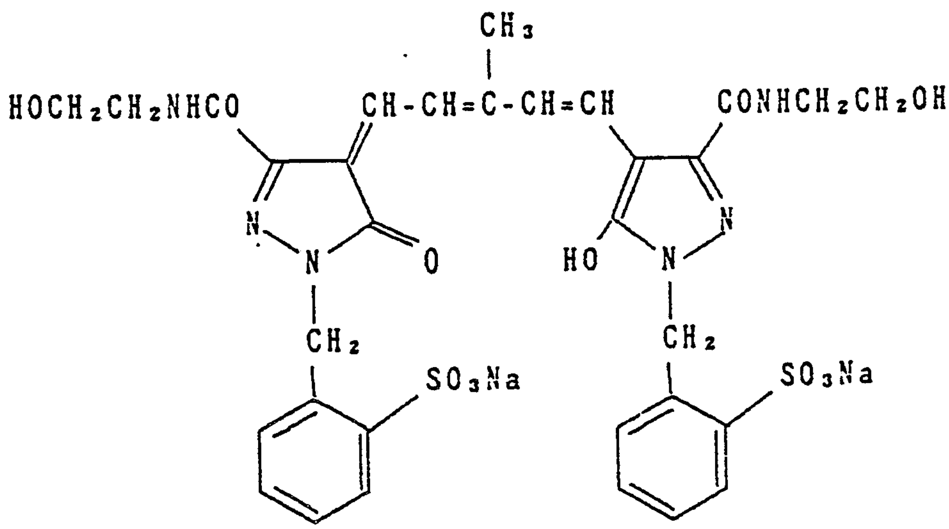


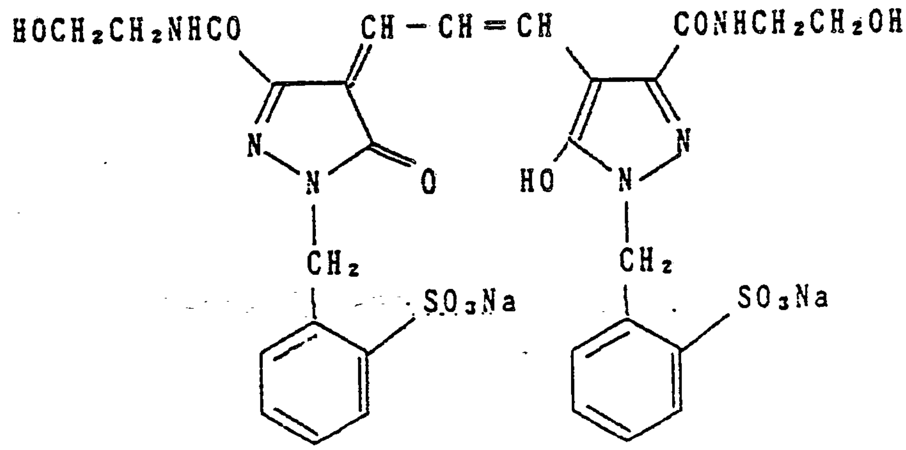
I－35



I－36



I－37



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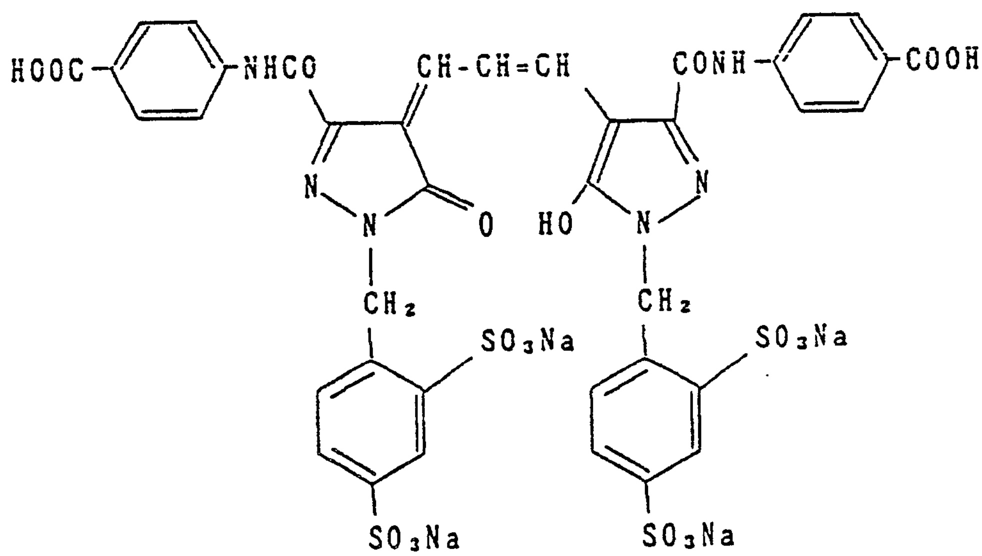

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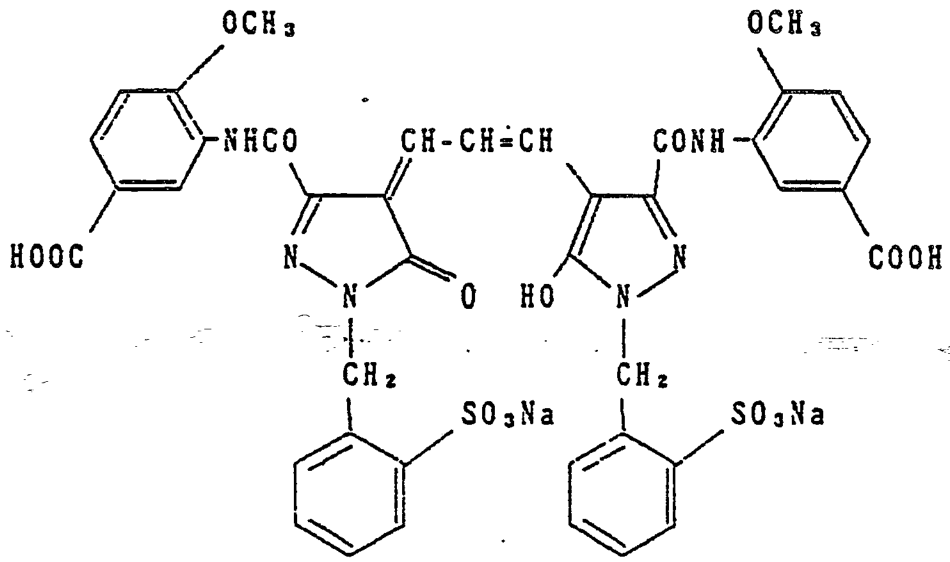
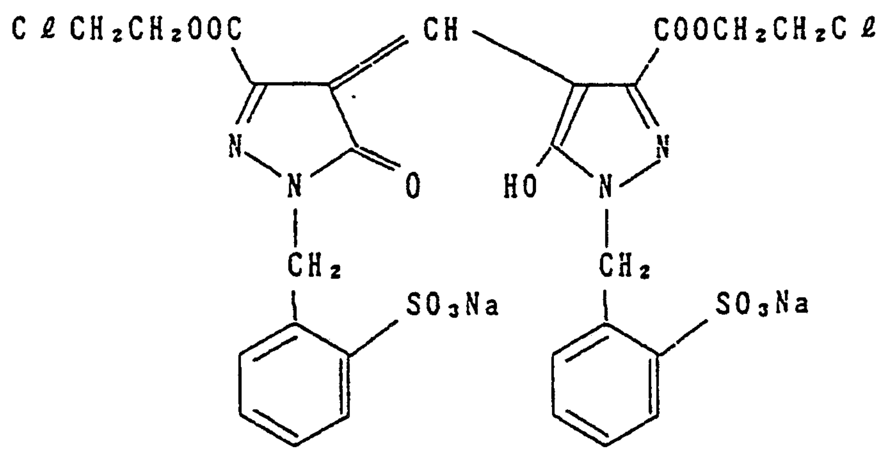
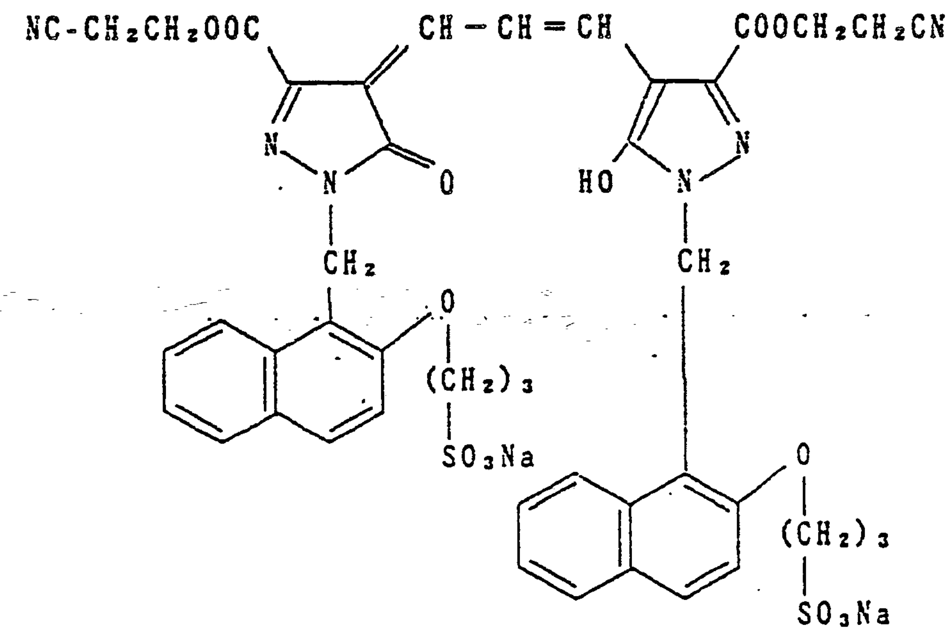


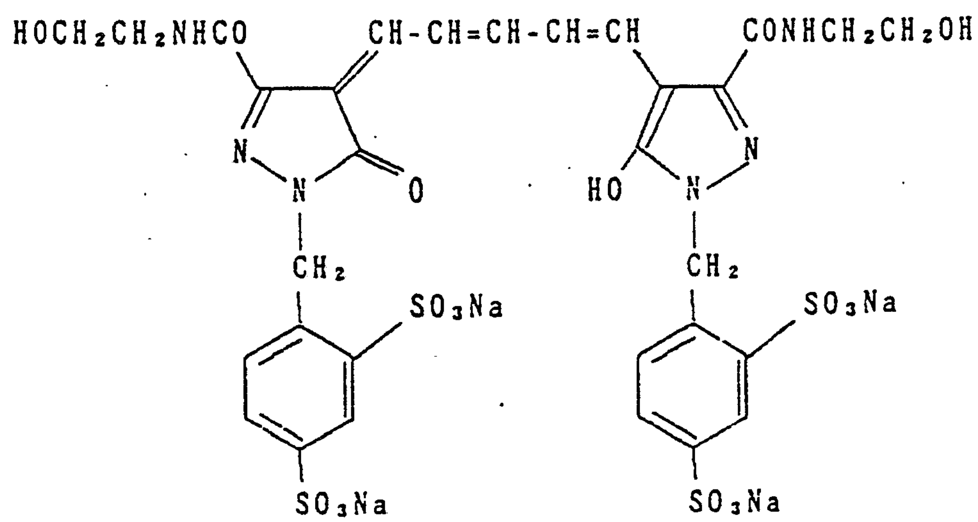
I－40



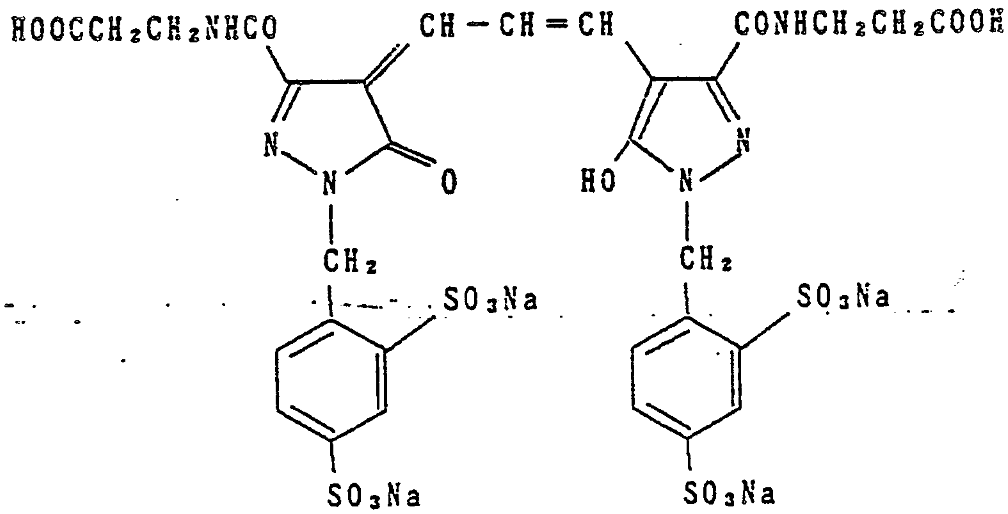
I - 4 1



I - 4 2



I - 43



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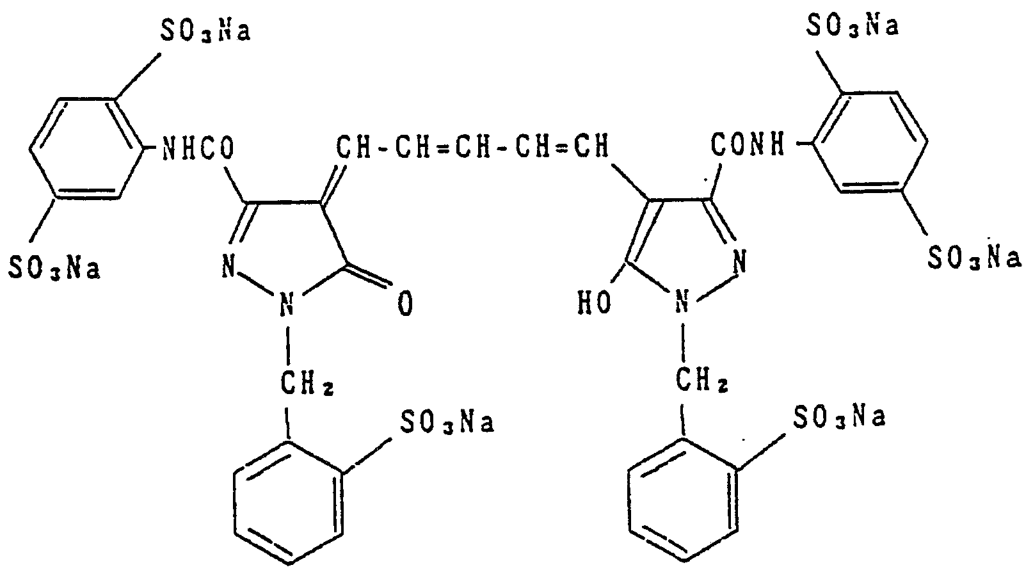
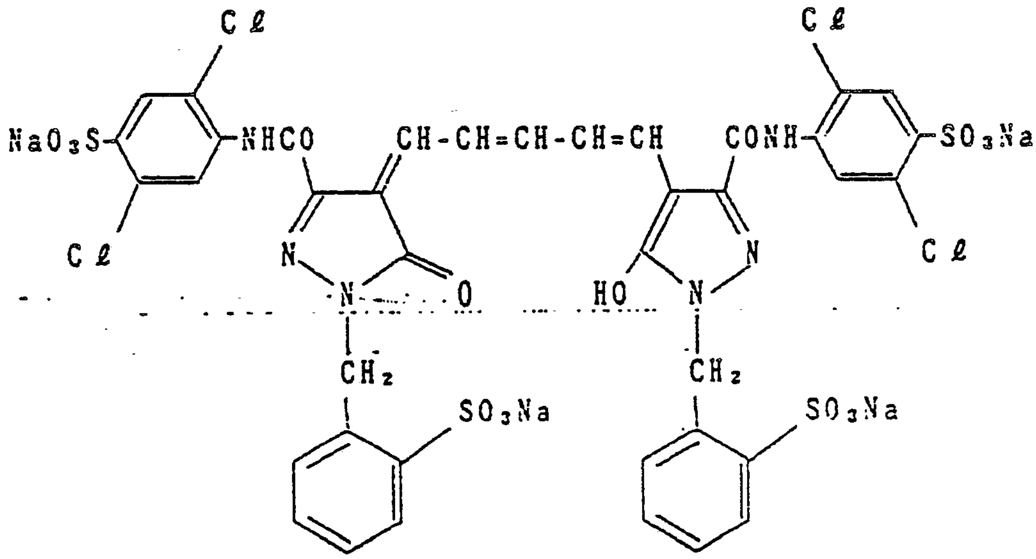


I - 4 5


C ℓ
C ℓ
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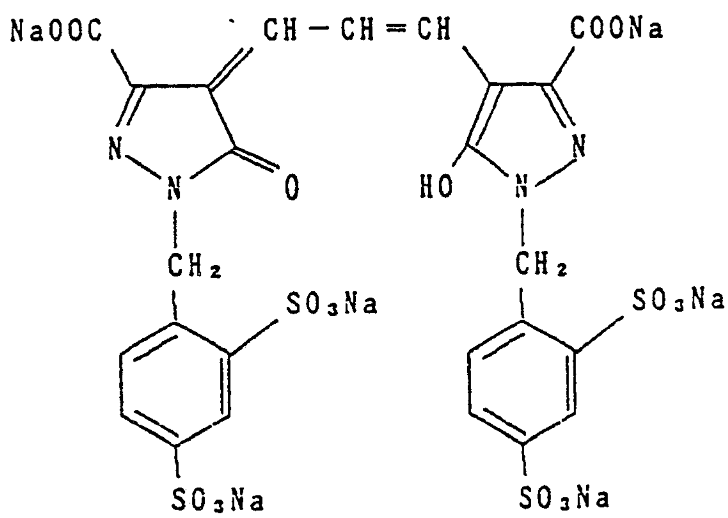
NHCO
CH-CH=CH-CH=CH
CONH
SO₃Na
C ℓ
C ℓ
N
N
O
HO
N
N
CH₂
CH₂
SO₃Na
SO₃Na

I - 4 6


NaOOC
CH — CH = CH
COONa
N
N
O
HO
N
N
CH₂
CH₂
SO₃Na
SO₃Na
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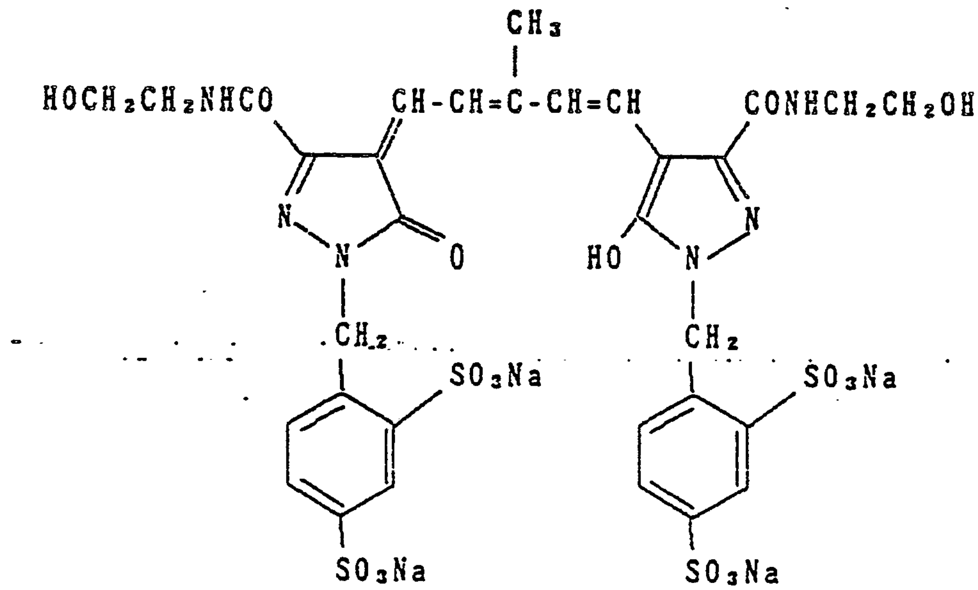
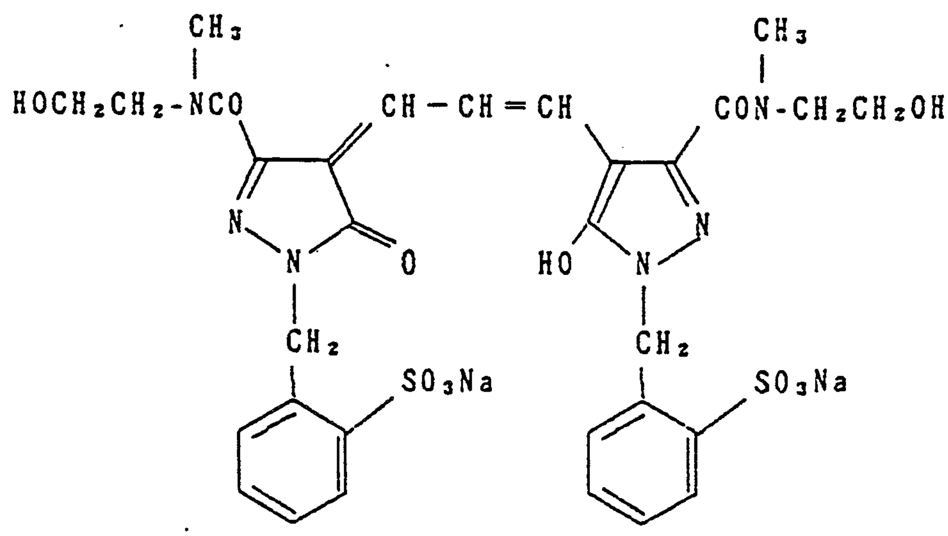
SO₃Na

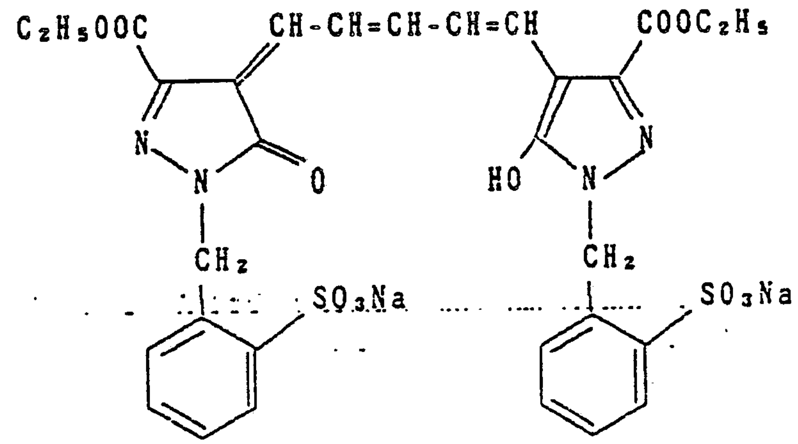
I － 4 7



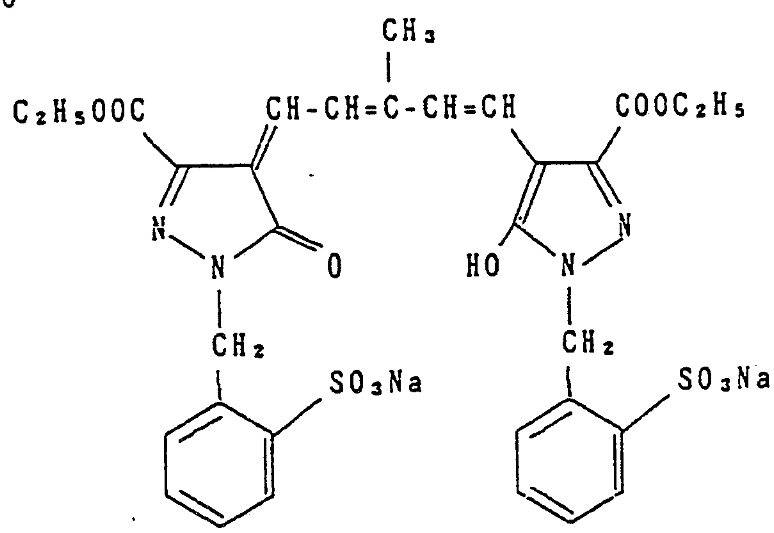
I － 4 8



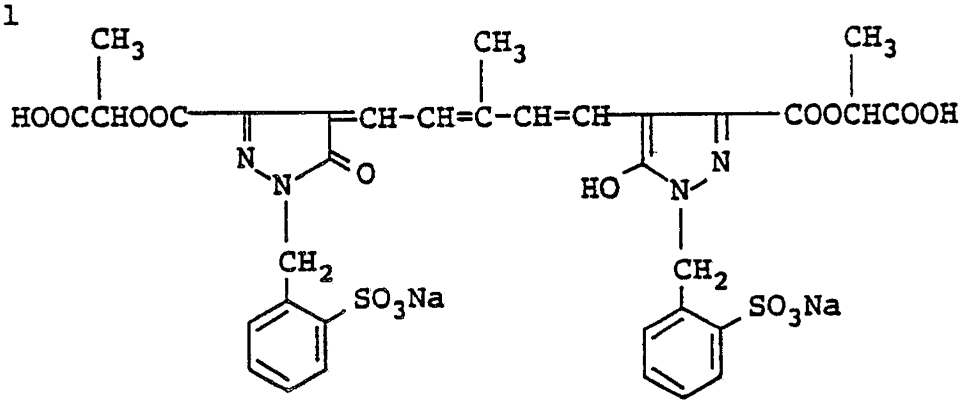
I - 4 9



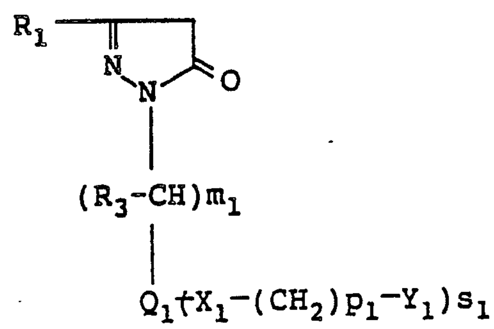
I - 5 0



I-51

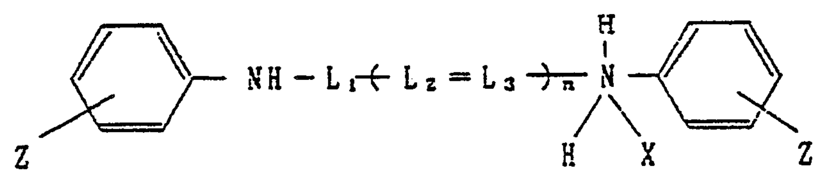


The compounds of formula (I) can be synthesized by various methods, for example, by carrying out the condensation of a pyrazolone represented by formula (III) and a compound represented by formula (IVa), (IVb), (IVc), (IVd) or (IVe) in the presence of bases:



(III)

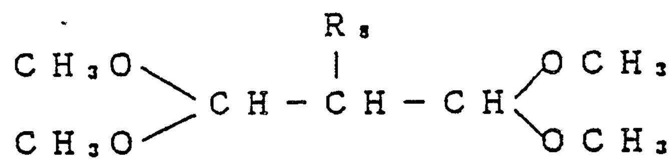
(IVa)



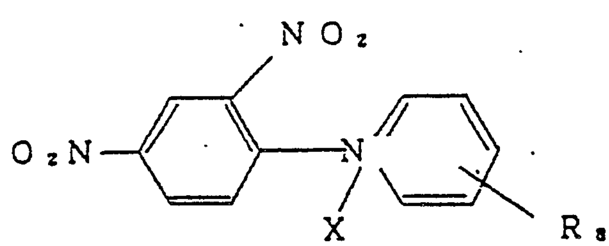
(IVb)

$HC(OC_2H_5)_3$

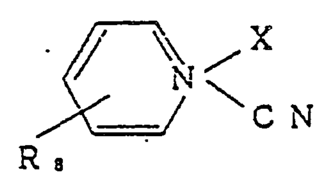
(IVc)



(IVd)



(IVe)



wherein R_1, R_3, Q_1, X_1, Y_1, L_1, L_2, L_3, m_1, n, p_1 and s_1 have the same definition as given above; Z represents hydrogen, a nitro group, or a halogen atom (e.g., chlorine, bromine); R_8 represents hydrogen, an alkyl group (e.g., methyl, ethyl), or a phenyl group; and X represents an anion (e.g., chloride, bromide, iodide, perchlorate, methyl sulfate, ethyl sulfate, p-toluene sulfonate). The other compounds of those represented by formula (I) can be synthesized by a similar manner to the above-described method.

Examples of bases which are used in the condensation reaction include pyridine, piperidine, triethylamine, triethanol amine, sodium acetate, and potassium acetate.

Examples of solvents which are used for carrying out the condensation reaction include alcohols (e.g., methanol, ethanol, isopropanol), amides (e.g., dimethylformamide, dimethylacetamide, N-methylpyrrolidone), nitriles (e.g., acetonitrile), dimethylsulfoxide, ethylene glycol, ethers (e.g., ethylene glycol monomethylether, ethylene glycol diethylether), water, and a mixture of water and the above-described solvents. The amount of the solvent in the mixture is preferably from 1 to 100 parts by volume per part by volume of water.

The reaction temperature may be selected from the range of from 0 °C to the boiling point of the solvent.

The reaction time is decided depending on the reaction temperature, and it is usually selected from the range of from about 30 minutes to about 3 days.

A pyrazolone represented by formula (III) is used in the condensation reaction in an amount of from 0.1 to 3 moles per mole of a compound represented by formula (IVa), (IVb), (IVC), (IVd) or (IVe).

The following is a description of the synthesis examples for the compounds represented by formula (I).

Synthesis Example 1 (Compound 3)

To 50 ml of ethanol were added 5.2 g of 3-ethoxycarbonyl-1-(2-sulfobenzyl)pyrazoline-5-one, then 4.2 ml of triethylamine, and 1.5 g of malondialdehyde dianilate. The mixture was heated and refluxed for 3 hours to obtain a uniform solution. To this hot solution was added a solution prepared by dissolving 1.2 g of sodium acetate in 15 ml of methanol with stirring. Then, 25 ml of isopropanol was added to the above solution to deposit a dark purple crystal. This crystal was filtered out, washed with isopropanol, and dried to yield 2 g of Compound 3.

Melting point: higher than 300 °C

$\lambda_{max}^{H_2O}$: 551 nm ϵ: 6.73×10^4

(ϵ: extinction exponent)

Synthesis Example 2 (Compound 8)

A mixture consisiting of 7.4 g of 3-carboxy-1-(2-sulfobenzyl)pyrazoline-5-one, 50 ml of methanol, and 7.5 ml of triethylamine was prepared and cooled with ice. To this mixture was added 2.8 g of glutaraldehyde dianil hydrochloride with stirring for 3 hours. To this solution was added a solution prepared by dissolving 4.2 g of sodium acetate in 50 ml of methanol and further 25 ml of isopropanol to deposit a dark purple crystal. To crystal was filtered out, washed with isopropanol, and dried to yield 5.4 g of Compound 8.

Melting point: higher than 300 °C

$\lambda_{max}^{H_2O}$: 626 nm ϵ: 7.89×10^4

The compounds which are represented by formula (II) are nondiffusible cyan couplers.

Synthesis Example 3 (Compound 10)

A mixture consisiting of 8 g of 3-(2-hydroxyethyl carbamoyl)-1-(2-sulfobenzyl)pyrazoline, 30 ml of methanol and 3.8 ml of triethylamine was prepared and cooled. To this solution were added 3 g of glutaraldehyde dianilate and then 2 ml of acetic anhydride. The mixture was reacted at room temperature for one hour, and then 20 ml of isopropanol was added to deposit a black crystal. The crystal was filtered out, washed with isopropanol, and dried to yield 6.1 g of Compound 10.

Melting point: higher than 300 °C

$\lambda^{H_2O}_{max}$: 633 nm ϵ: 8.8×10^4

Synthesis Example 4 (Compound 18)

A mixture consisting of 8 g of 3-carboxy-1-[2-(4-sulfophenyl)ethyl]pyrazoline-5-one, 50 ml of methanol, and 7 ml of triethylamine was prepared, and then 1.6 g of N,N′-diphenylformamidine hydrochloride was added and heated for 2 hours to produce a uniform solution. To this solution were added a solution prepared by dissolving 4.5 g of sodium acetate in 50 ml of methanol and further 20 ml of isopropanol to deposit a yellow crystal. This crystal was filtered out, washed with isopropanol and dried to yield 4 g of Compound 18. Melting point: higher than 300 °C

$\lambda^{H_2O}_{max}$: 452 nm ϵ: 2.10×10^4

Synthesis Example 5 (Compound 12)

Compound 12 was obtained by using 3-ethoxycarbonyl-1-(2,4-disulfobenzyl)pyrazoline-5-one in the same manner as Synthesis Example 2.
Melting point: higher than 300 °C

$\lambda^{H_2O}_{max}$: 640 nm ϵ: 7.02×10^4

Synthesis Example 6 (Compound 20)

Compound 20 was obtained by using 3-carboxy-1-[2-(4-sulfobutyloxy)benzyl]pyrazoline-5-one in the same manner fas Synthesis Example 2.
Melting point: 264 to 269 °C (decomposition)

$\lambda^{H_2O}_{max}$: 628 nm ϵ: 7.39×10^4

The compounds which are represented by formula (II) are nondiffusible cyan couplers.

The following is the detailed description of compounds according to formula (II).

In formula (II), R_8 represents a chain or cyclic aliphatic group, preferably having from 1 to 32 (total) carbon atoms (e.g., methyl, butyl, pentadecyl, cyclohexyl), an aromatic group, preferably having from 6 to 32 (total) carbon atoms (e.g., phenyl, naphthyl), a heterocyclic group, preferably 5~7-membered ring containing at least one of N, O and S atoms as hetero atom (e.g., 2-pyridyl, 3-pyridyl, 2-furanyl, 2-oxazolyl) or a substituted amino group, preferably substituted with at least one of an alkyl and aryl groups. These groups may be substituted by a substituent selected from an alkyl group, an aryl group, an alkoxy or aryloxy group, (e.g., methoxy, dodecyloxy, methoxyethoxy, phenyloxy, 2,4-di-tert-amylphenoxy, 3-tertbutyl-4-hydroxyphenyloxy, naphthyloxy), a carboxyl group, an alkylcarbonyl or arylcarbonyl group (e.g., acetyl, tetradecanoyl, benzoyl), an alkoxycarbonyl or aryloxycarbonyl group (e.g., methoxycarbonyl, benzyloxycarbonyl, phenoxycarbonyl), an aliphatic or aromatic acyloxy group (e.g., acetyl, benzoyloxy, phenylcarbonyloxy), an aliphatic or aromatic sulfamoyl group (e.g., N-ethylsulfamoyl, N-octadecylsulfamoyl), an aliphatic or aromatic carbamoyl group (e.g., N-ethylcarbamoyl, N-methyldodecylcarbamoyl), an aliphatic or aromatic sulfonamido group (e.g., methane sulfonamido, benzenesulfonamido), an aliphatic or aromatic acylamino group (e.g., acetylamino, benzamido, ethoxycarbonylamino, phenylaminocarbonylamino), an imido group (e.g., succinimido, hydantoinyl), an aliphatic or aromatic sulfonyl group (e.g., methanesulfonyl,, a hydroxy group, a cyano group, a nitro group and a halogen atom.

In the specification of the present invention, the term "an aliphatic group" means a straight-chain, branched-chain, or cyclic aliphatic hydrocarbon group, which may be a saturated or unsaturated group such as an alkyl, alkenyl or alkynyl group.

In formula (II), R_7 represents a C_2 to C_{20} total) alkyl group (e.g., ethyl, butyl, pentadecyl) or an aliphatic or aromatic acylamino group (e.g., tetradecanoylamino, benzolylamino, 2-(2,4-di-tert-amylphenoxy)-butaneamido.

In formula (II), X_3 represents hydrogen, a halogen atom (e.g., Cl, Br, F), an aliphatic group (e.g., methyl, propyl, allyl), an alkoxy group (e.g., methoxy, butoxy), or an aliphatic or aromatic acylamino group (e.g., acetoamide).

In formula (II), R_7 and X_3 together may form a nonmetallic atomic group necessary for forming a 5-, 6- or 7-membered ring, such as a carbon ring and a heterocyclic ring preferably containing at least one of N, O, and S atoms as a hetero atom (e.g., benzene ring, lactam ring).

In formula (II), Z represents hydrogen or a coupling-releasing group, such as halogen atom (e.g., fluorine, chlorine, bromine), an alkoxy group (e.g., ethoxy, dodecyloxy, methoxycarbamoylmethoxy, carboxypropyloxy, methylsulfonylethoxy), an aryloxy group (e.g., 4-chlorophenoxy, 4-methoxyphenoxy, 4-carboxyphenoxy), an aliphatic or aromatic acyloxy group (e.g., acetoxy, tetradecanoyloxy, benzoyloxy), an aliphatic or aromatic sulfonyloxy group (e.g., methanesulfonyloxy, toluenesulfonyloxy), an amido group (e.g., dichloroacetylamino, heptabutyrylamino, methanesulfonylamino, toluenesulfonylamino), an alkoxy carbonyloxy group (e.g., ethoxycarbonyloxy, benzyloxycarbonyloxy), an aryloxycarbonyloxy group (e.g., phenoxycarbonyloxy), an aliphatic or aromatic thio group (e.g., ethylthio, phenylthio), a heterocyclic ring thio group (e.g., tetrazolylthio), an imido group (e.g., succinimido, hydantoinyl), and a heterocyclic ring containing at least one N atom (e.g., 1-pyrazolyl, 1-benztriazolyl), an aromatic azo group (e.g., phenylazo). These releasing groups may contain photographically useful groups.

In formula (II), R_7 is preferably a C_2 to C_{15} alkyl group, more preferably a C_2 to C_4 alkyl group.

In formula (II), Z is preferably hydrogen or a halogen atom, more preferably a halogen atom.

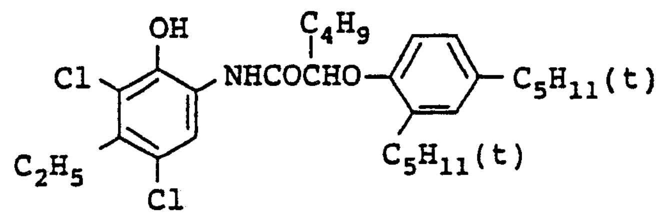
In formula (II), X_3 is preferably a halogen atom.

In formula (II), a ring formed by the ring closure of R_7 and X_3 is preferably a 5-membered oxindol ring.

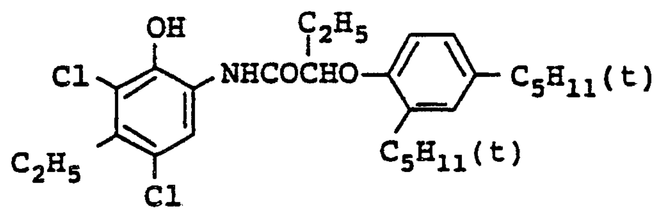
The compounds represented by formula (II) and synthetic methods thereof are disclosed, for example, in U.S. Patents 4,564,590, 2,895,826, 4,557,999, 4,565,777, 4,124,396, 4,613,564, 4,327,173, 4,564,586 and 4,430,423, JP-A-61-39045, JP-A-62-70846, JP-A-61-390441 and JP-A-62-257158.

The following are examples of compounds represented by formula (II) of the present invention without restricting the scope of the invention.

(C-1)



(C-2)



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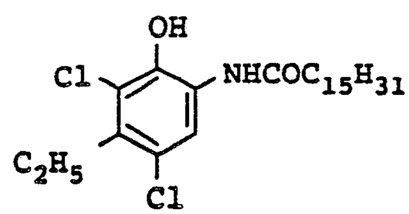
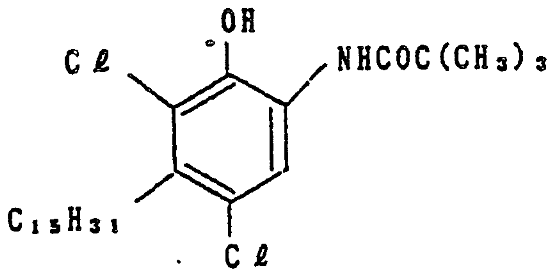


(C－4)



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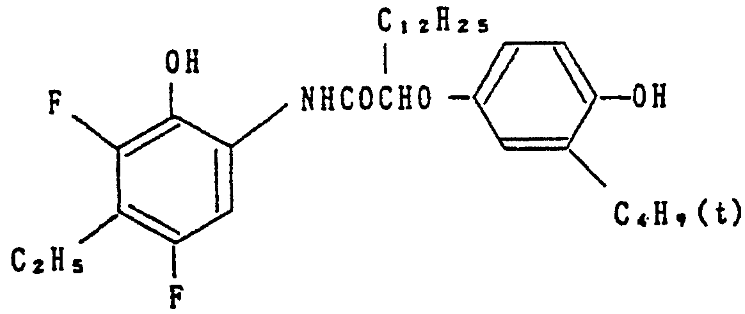

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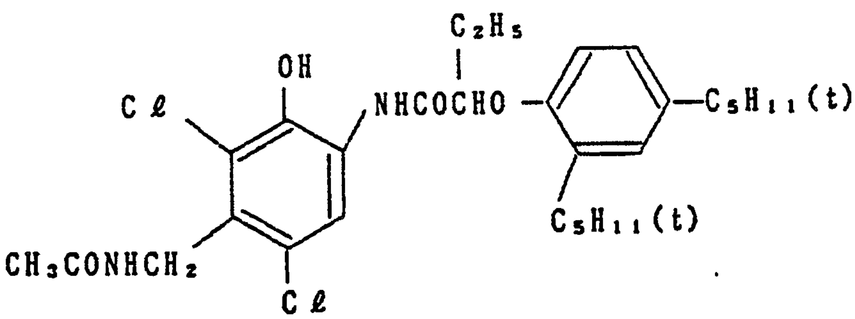
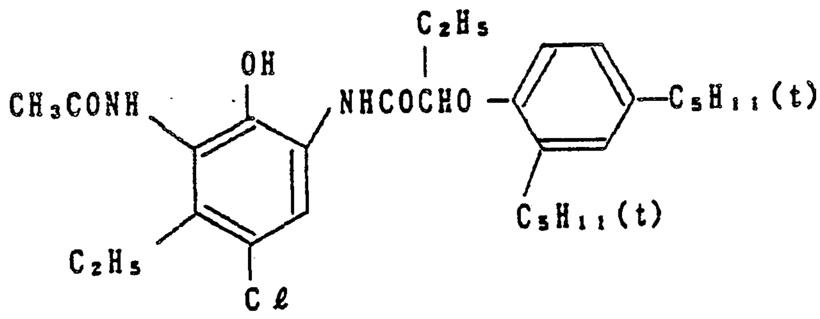


(C − 7)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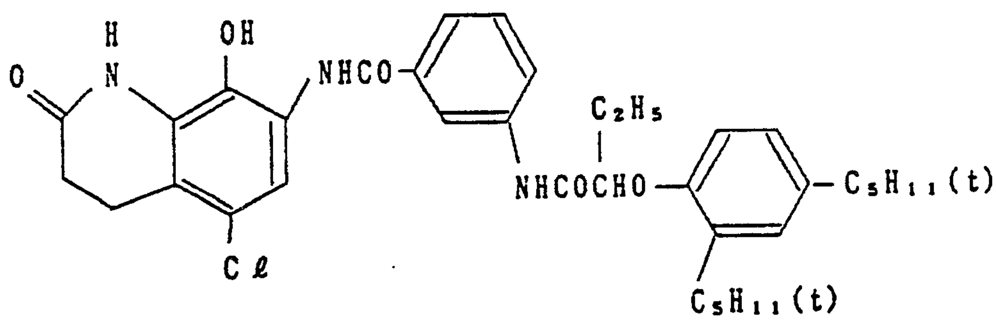
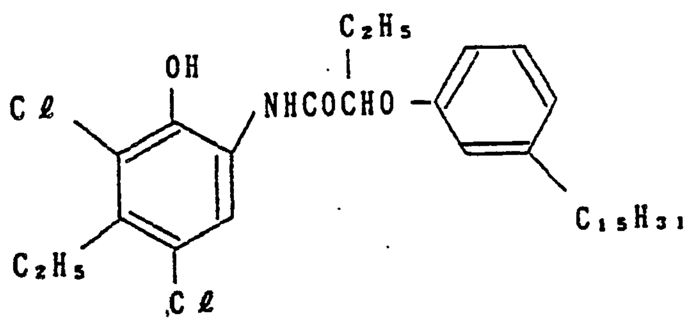
C5H11(t)
C2H5
Cℓ

(C − 8)


H
OH
O
N
NHCO
C2H5
NHCOCHO
C5H11(t)
Cℓ
C5H11(t)

(C − 9)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Cℓ
NHCOCHO
C15H31
C2H5
Cℓ

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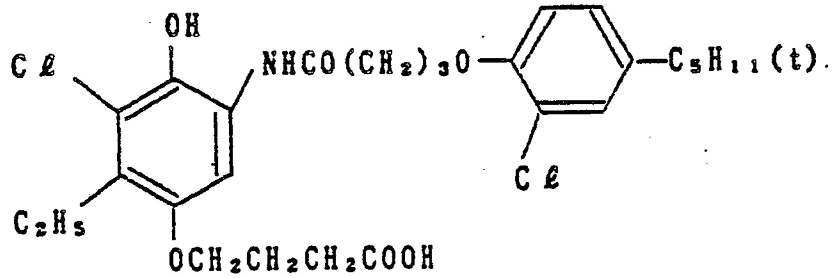
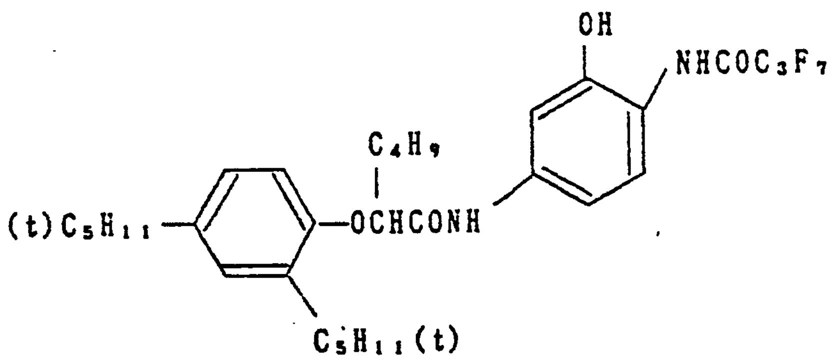

OH
Cℓ
NHCO(CH₂)₃O
C₅H₁₁(t)
Cℓ
C₂H₅
OCH₂CH₂CH₂COOH

(C - 1 1)


OH
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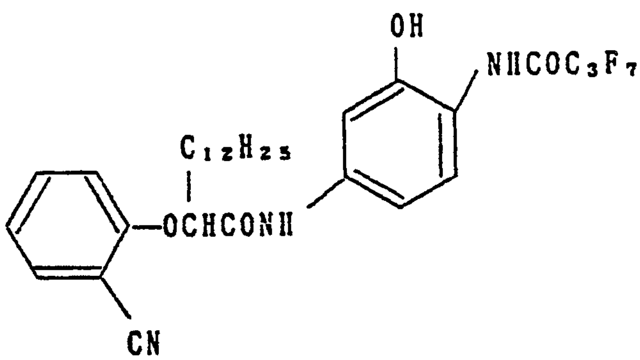
C₄H₉
(t)C₅H₁₁
OCHCONH
C₅H₁₁(t)

(C - 1 2)


OH
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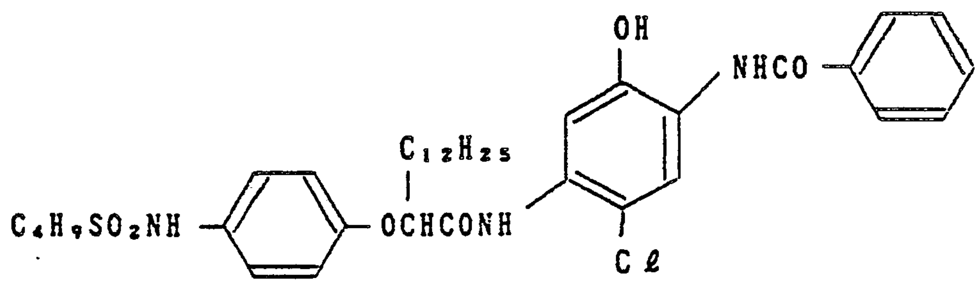
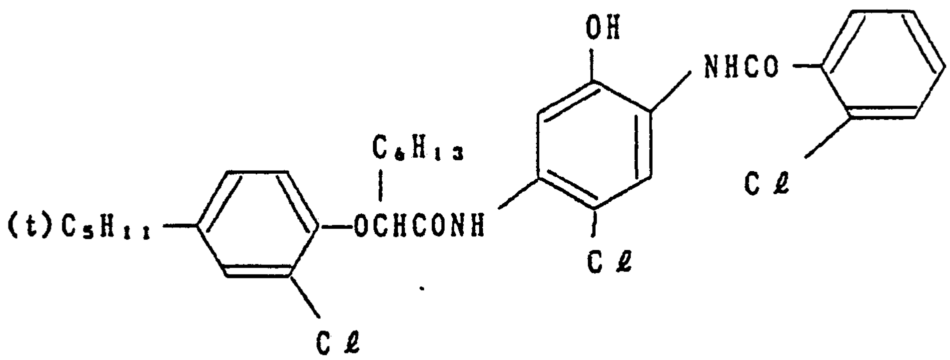
OCHCONH
CN

(C－13)



(C－14)



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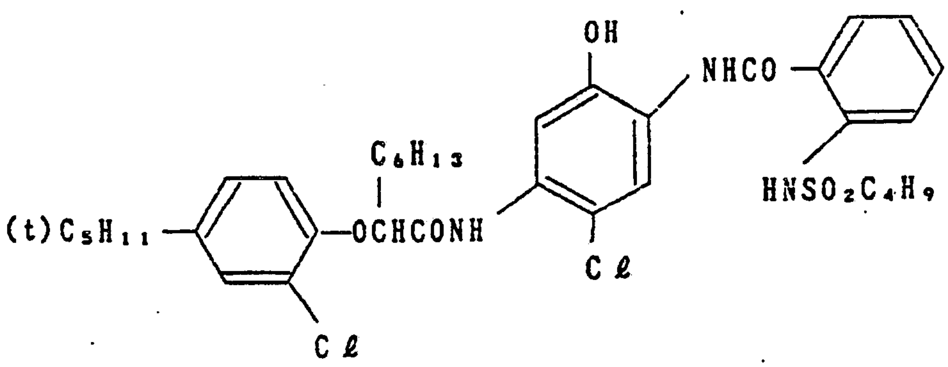

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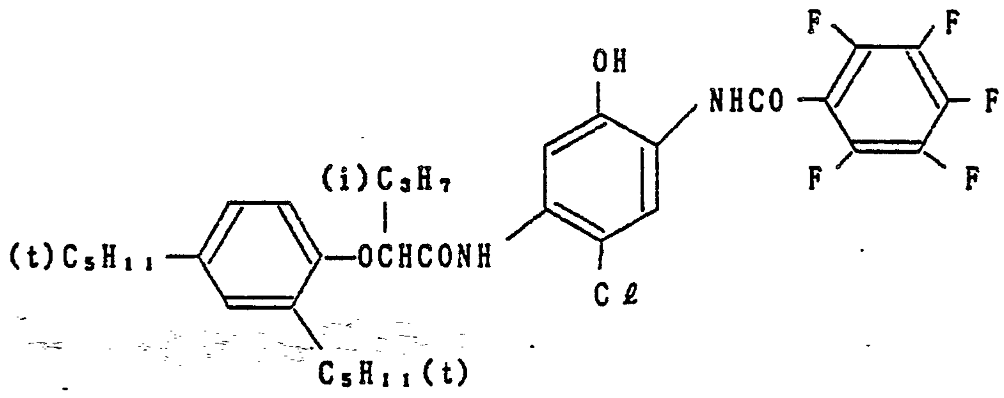
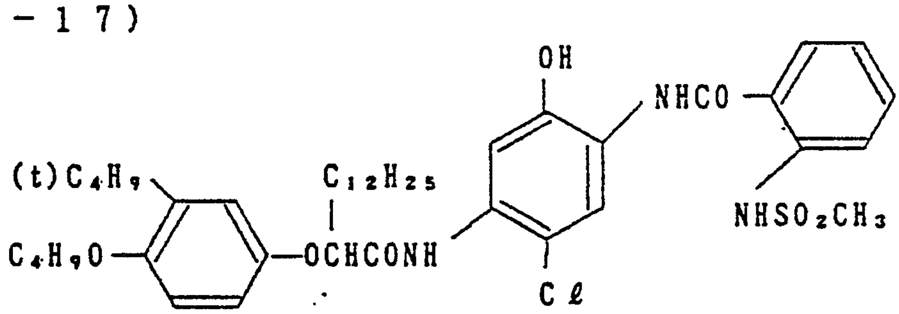

OH
NHCO
F
F
F
F
F
(i)C3H7
(t)C5H11
OCHCONH
Cℓ
C5H11(t)

(C－17)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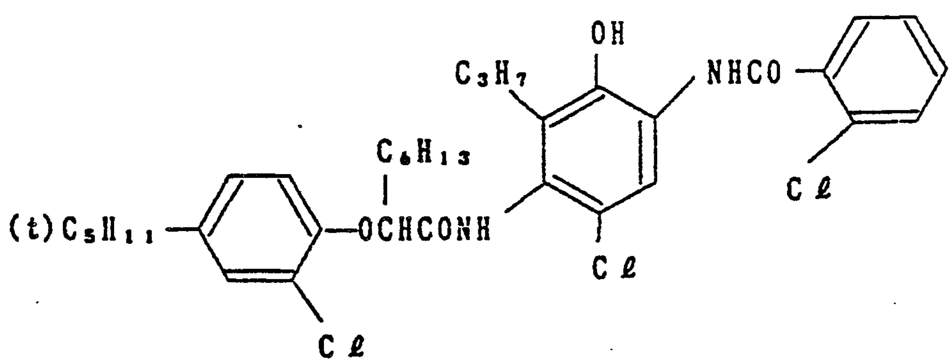
C4H9O
OCHCONH
Cℓ

(C－18)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Cℓ
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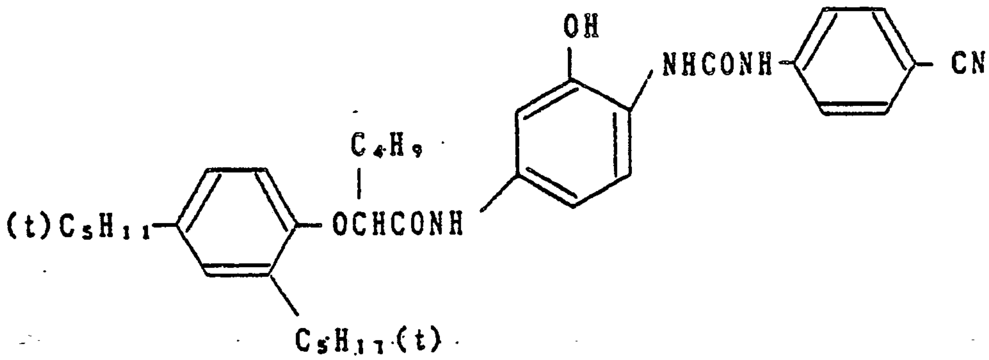
OCHCONH
Cℓ
Cℓ

(C - 19)



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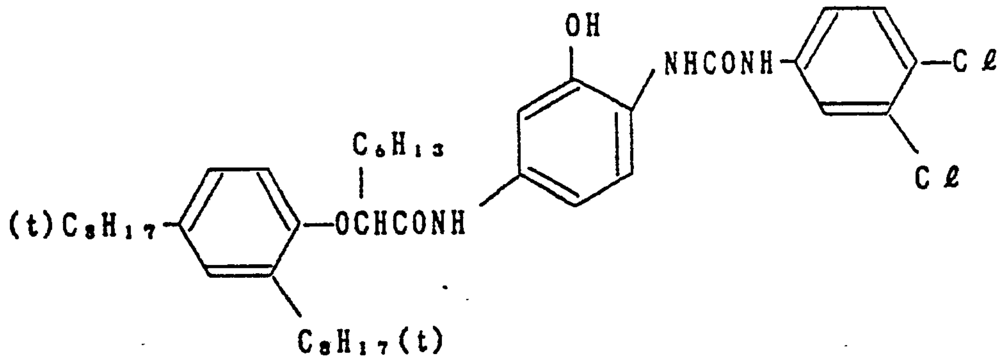

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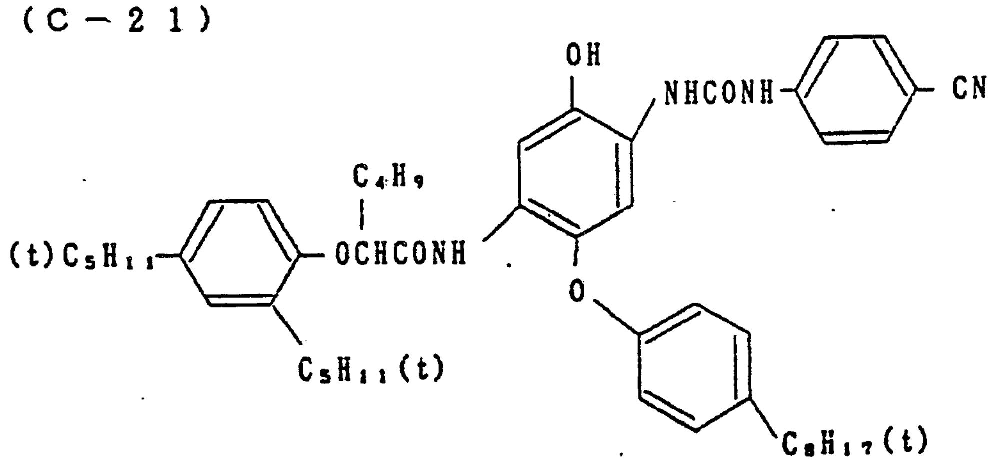

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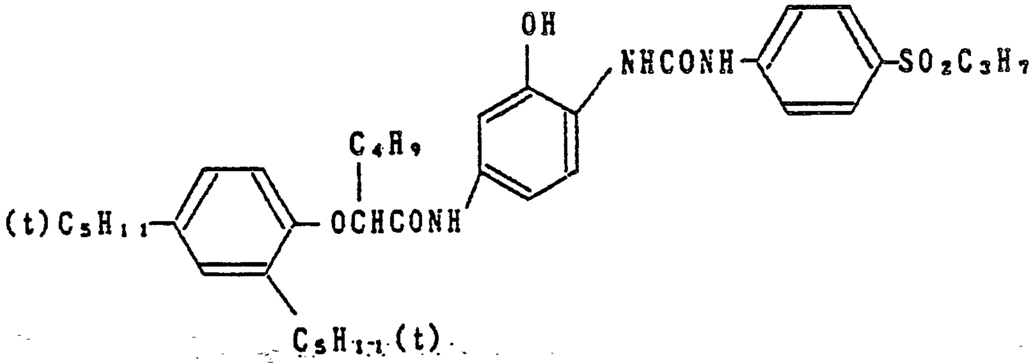

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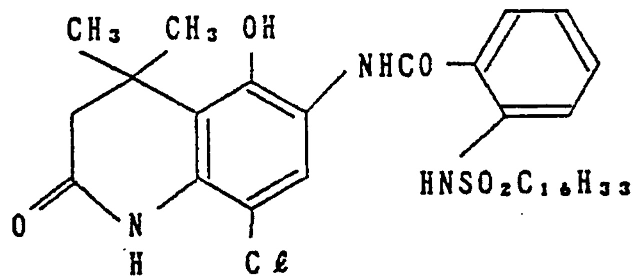

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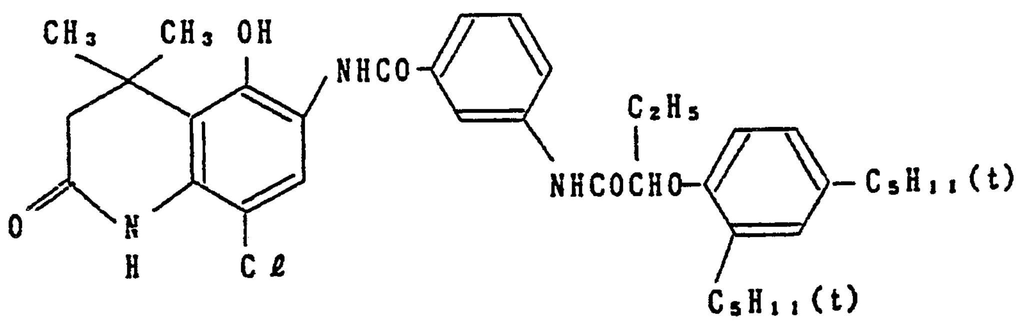
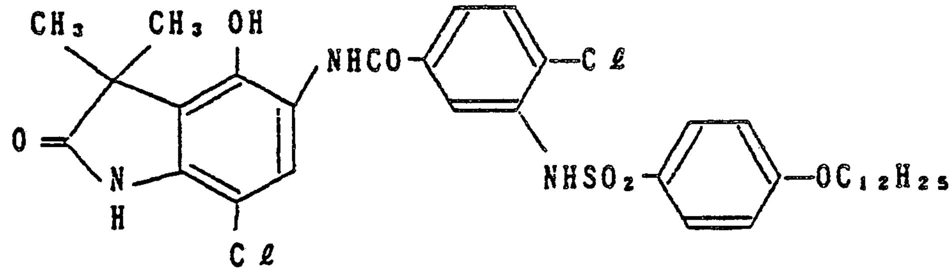
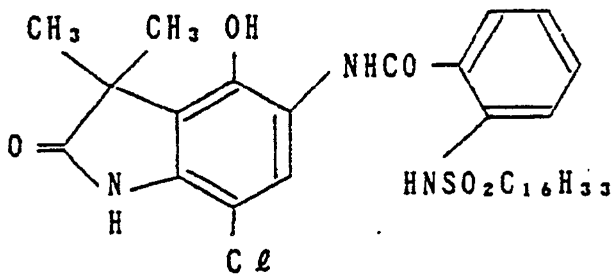


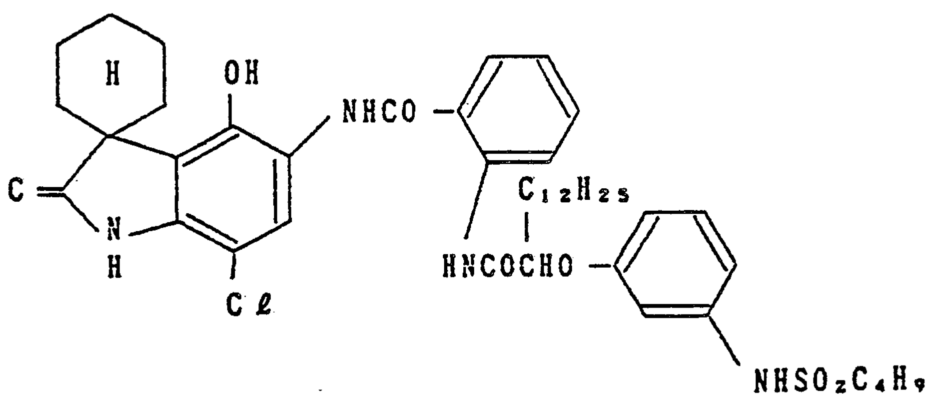
(C－25)



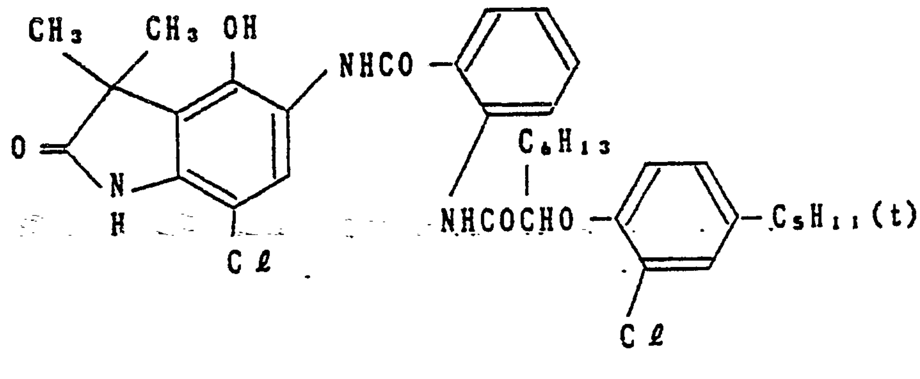
(C－26)



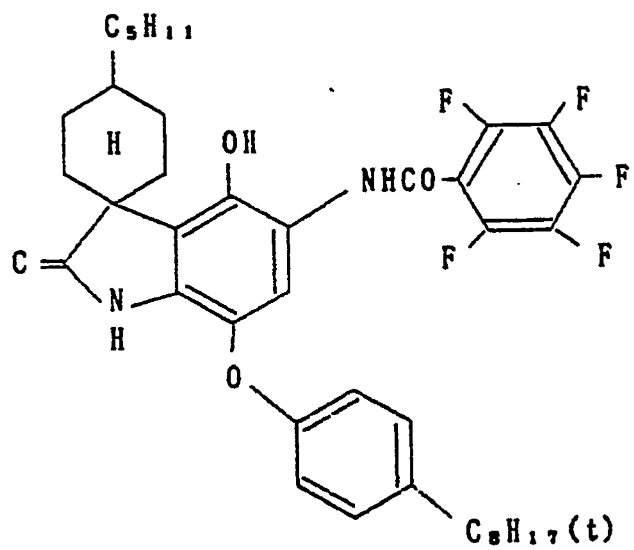
(C－27)



(C-28)



(C-29)



The dyes of formula (I) can be used as filter dyes, irradiation-preventing dyes or antihalation dyes in any effective amount, preferably in such an amount that the dye provides optical density (of whole hydrophilic colloid layers) of 0.05 to 3.0. The addition thereof is conducted in any step of processing before coating a photographic layer coating composition onto a support.

In order to out spectral absorption which is harmful to spectral sensitizers it is preferable to use a dye represented by formula (I) wherein n = 1 for a green sensitizing dye, and a dye represented by formula (I) wherein n = 2 for a red sensitizing dye.

The dyes of the present invention can be dispersed in at least one of hydrophilic colloidal layers, i.e., emulsion layers and the other hydrophilic colloidal layers (intermediate layer, protective layer, antihalation layer including backing layer, and filter layers) by various known methods.

(1) A method of dissolving or dispersing the dyes of the present invention directly in coating compositions of emulsion layers and hydrophilic colloidal layers, or a method of dissolving or dispersing the dyes of the present invention in an aqueous solution or a solvent and then using the resulting solution or

dispersion in emulsion layers and hydrophilic colloidal layers. The dyes of the present invention can be dissolved in a suitable solvent, for example, methyl alcohol, ethyl alcohol, propyl alcohol, methyl cellosolve, halogenated alcohol (described in JP-A-48-9715 and U.S. Patent 3,756,830), acetone, water, pyridine or mixtures thereof, and the resulting solution may be added to emulsions or a hydrophilic colloidal sulution.

(2) A method of placing a hydrophilic copolymer having the opposite electric charge to the dye ion in layers as a mordant and localizing the dyes in the specific layers by the interaction between the polymer and the dye molecules.

The term "polymer mordants: means polymers containing secondary and tertiary amino groups, polymers having a nitrogen-containing heterocyclic portion, and polymers containing these quaternary cationic groups, having a molecular weight of 5,000 or more, most preferably 10,000 or more.

Suitable mordants include, for example, vinyl pyridine polymers and vinyl pyridinium cation polymer described in U.S. Patent 2,548,564; vinyl imidazolium cation polymer described in U.S. Patent 4,124,386; polymer mordants which are able to cross-link with gelatin, disclosed in U.S. Patent 3,625,694; aqueous sol-type mordants disclosed in U.S. Patent 3,958,995 and JP-A-54-115228; water-insoluble mordants disclosed in U.S. Patent 3,898,088; reactive mordants which can be covalently bonded with the dyes, disclosed in U.S. Patent 4,168,976; polymers derived from an ethylenically unsaturated compound having a dialkylaminoalkylester residue as described in British Patent 685,475; products resulting from the reaction of polyvinyl alkylketone and aminoguanidine as described in British Patent 850,281; and polymers derived from 2-methyl-1-vinylimidazole as described in U.S. Patent 3,445,231.

(3) A method of dissolving compounds using surfactants. The surfactants may be oligomers or polymers.

A detailed description of the above-described oligomers and the polymers is given in the specification of JP-A-60-158437, pp. 19 to 27 (filed January 26, 1984, by Fuji Photo Film Co., Ltd.). Also the hydrozol of a lipophilic polymer as described in JP-B-51-39835 may be added to the above-obtained hydrophilic colloidal dispersion.

The cyan coupler represented by formula (II) can be employed in an amount of 0.1 to 1 mol, preferably 0.2 to 0.5 mols per mol of silver halide in the photographic silver halide emulsion layer containing the cyan coupler.

The cyan couplers represented by formula (II) are dissolved in high-boiling organic solvents (e.g., phthalic acid ester solvents, phosphate solvents, fatty acid ester solvents) and the resulting solutions are dispersed in hydrophilic colloidal media to be added to silver halide emulsions.

In order to improve the properties of the silver halide color photographic materials in storage, there can be added benzotriazole ultraviolet absorbing agents and substantially water-insoluble, organic solvent-soluble polymers. In particular, the use of these polymers is effective for improving dark discoloration. As the most useful polymers, there are mentioned those described in Japanese Patent Application No. 61-162813.

The hydrophilic colloids include typically gelatin and also any other conventionally known ones to be used for photographic materials.

The present invention can employ any of silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide, and silver chloride as a silver halide. For the purpose of rapid processing, in particular, silver chlorobromide containing 90 mol% or more of silver chloride (preferably 98 mol% or more) is favorable. This silver chlorobromide may contain a little silver iodide but preferably contains no silver iodide.

The grains of silver halide of the present invention may be in the form of regular crystals such as a cube and an octahedron or irregular crystals such as a sphere and a tabular or combinations thereof. Also, a mixture of grains having various forms of crystals can be used, but those in the form of regular crystals are preferably used.

The silver halide grains of the present invention may consist of different phases or a uniform phase as to the inside layer and the surface layer. Also, the grains may be those which form latent images mainly on the surface thereof (e.g., negative emulsion) or mainly in the inside thereof (e.g., internal latent image emulsion, previously fogged direct reversal emulsion). Preferably, the grains are those which can form latent images mainly on the surface thereof.

The silver halide emulsions to be used in the present invention are preferably tabular grain emulsions in which the grains having a thickness of 0.5 µm or less, preferably 0.3 µm or less, a diameter of preferably 0.6 µm or more and an average aspect ratio of 5 or more occupy 50% or more of the whole projected area, or monodisperse emulsions such that the statistical coefficient of variation (a value of $s/\bar{d}$ obtained by dividing the standard deviation s by a diameter $\bar{d}$ in the distribution represented by a diameter of a circle approximate to the projected areas) is 20% or less. Also, two or more of tabular grain emulsions and monodisperse emulsions may be mixed.

The photographic emulsions to be used in the present invention can be prepared by the methods described in P. Glafkides, "Chimie er physique Photographique", (Paul Montel Co., Ltd., 1967), G.F. Duffin, "Photographic Emulsion Chemistry" (Focal Press, 1966), and V.L. Zelikman, "Making and Coating Photographic Emulsion" (Focal Press, 1964).

In order to control the growth of grains when forming silver halide grains, there can be used silver halide solvents, for example, ammonia, potassium thiocyanate, ammonium thiocyanate, thioether compounds (e.g., U.S. Patent 3,271,157; 3,574,628; 3,704,130; 4,297,439; 4,276,374), thion compounds (e.g., JP-A-53-144319, JP-A-53-82408, JP-A-55-77737), and amine compounds (e.g., JP-A-54-100717).

In the process of forming or physically ripening silver halide grains, there may be present a cadmium salt, zinc salt, thallium salt, iridium salt or complex salt thereof, rhodium salt or complex salt thereof, or ferric salt or ferric complex salt thereof.

Silver halide emulsions are usually chemically sensitized, for example, by the methods described in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser, (Akademisch Verlagsgesellshaft, 1968) pp. 675 to 734.

Namely, there can be used a method of sulphur sensitization using compounds containing sulphur which can react with active gelatin or silver (e.g., thiosulfates, thioureas, mercapto compounds, rhodanines); a method of reduction sensitization using reducible materials (e.g., stannous salt, amines, hydrazine derivatives, formamidine sulfinic acid, silane compounds), and a method of noble metal sensitization using noble metal compounds (e.g., gold complexes and other complexes of metals belonging to Group VIII in the periodic table such as Pt, Ir and Pd) alone or in combination thereof.

In order to prevent photographic fog in the production step, preservation or processing of the photographic materials, or to stabilize the photographic properties, the silver halide photographic emulsions to be used in the present invention can contain various compounds, for example, azoles such as benzothiozolium salt, nitroindazoles, triazoles, benzotriazoles, and benzimidazoles (particularly, those with nitro- or halogen-substituents); heterocyclic mercapto compounds such as mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadioazoles, mercaptotetrazoles (particularly, 1-phenyl-5-meratptotetrazole), and mercaptopyrimidines; these heterocyclic mercapto compounds having water-soluble groups such as carboxyl group and sulfone group; thioketo compounds such as oxazolinethion; azaindenes such as tetraazindenes (particularly, 4-hydroxy-substituted (1,3,3a,7)tetraazaindenes); benzenethiosulfonic acids; and benzenesulfinic acids as antifoggants or stabilizers.

The silver halide photographic emulsions of the present invention can contain color couplers such as a cyan coupler, magenta coupler, yellow coupler and compounds for dispersing couplers.

Namely, the silver halide photographic emulsions of the present invention may contain compounds which form color by oxidation coupling with an aromatic primary amine developing agent (e.g., phenylenediamine derivatives, aminophenol derivatives) in color development. For example, there are 5-pyrazolone couplers, pyrazolobenzimidazole couplers, cyanoacetylcumarone couplers, pyrazolotriazole couplers, and open-chain acylacetonitrile couplers as magenta couplers and acylacetoamide couplers (e.g., benzoyl acetanilides, pivaloyl acetanilides) as yellow couplers.

These couplers are preferably nondiffusible couplers having hydrophobic groups called ballast groups in the molecule. The couplers may be 4 equivalent or 2 equivalent to a silver ion, or colored couplers having the effect of color correction, or couplers releasing development restrainers along with the development (the so-called DIR couplers).

The couplers other than DIR couplers may contain colorless DIR coupling compounds which form colorless products from the coupling reaction and release development restrainers. Also, there may be added ultraviolet absorbing agents and discoloration-preventing agents such as cinnamic acid esters and 2-(2-hydroxyphenyl)benzotriazole.

These discoloration-preventing agents include compounds described in the following patent specifications:

U.S. Patents 3,432,300, 3,573,045; 3,574,627; 3,700,455; 3,764,337; 3,935,016; 4,254,216; 4,268,593; 4,430,425; 4,465,757; 4,465,765; 4,518,679; British Patent 1,347,556; British Patent Unexamined Publication 2,066,975; JP-A-52-152225; JP-A-53-17729; JP-A-53-20327; JP-A-54-145530; JP-A-55-6321; JP-A-55-21004; JP-A-61-72246; JP-A-61-73152; JP-A-61-90155; JP-A-61-90156; and JP-A-61-145554.

The photographic emulsions of the present invention may contain, for example, polyalkylene oxide or derivatives thereof, such as ether, ester and amine; thioether compounds, thiomorpholines, quaternary ammonium salt compounds, urethane derivatives, urea derivatives, imidazole derivatives and 3-pyrazolidones so as to increase sensitivity and contrast or accelerate development.

The silver halide photographic emulsions of the present invention can employ known water-soluble dyes (e.g., oxonol dye; hemioxonol dye and merocyanine dye) in addition to the dyes disclosed in the present invention as filter dyes or irradiation-preventing dyes. Also, known cyanaine dyes, merocyanine dyes and hemicyanine dyes other than the dyes disclosed in the present invention may be used as spectral sensitizers.

The photographic emulsions of the present invention may contain various surfactants for the use as coating aids and antistatic agents, improving slipping-propertiers, emulsion-dispersing, preventing adhesion, and improving photographic characteristics (for example, accelerating development, providing high contrast, sensitizing). Also, the photographic materials of the present invention can contain various additives such as discoloration-preventing agents, hardening agents, color antifoggants, ultraviolet-absorbing agents, and protective colloids such as gelatin, which are described particularly in Research Disclosure Vol. 176, (1978, XII) RD-17643.

The finished emulsions are coated on a suitable support, for example, baryta paper, resin-coated paper, synthetic paper, triacetate film, polyethylene terephthalate film, or other plastic supports or glass plates.

The silver halide photographic materials of the present invention include color positive film, color paper, color negative film, color reversal film (which may contain couplers or may not), photographic materails for plate making processes (e.g., lith film, lith dupe film), photosensitive materials for cathode ray tube display (e.g., photosensitive materials for emulsion X-ray recording, direct or indirect photographing materials using a screen), photographic materials for a silver salt diffusion transfer process, photographic materials for a color diffusion transfer process, photographic materials for a dye transfer process, an inhibition transfer process, photographic materials for a silver dye bleach process, photographic materials for recording print-out images, photographic materials for direct printing of images, photographic materials for heat development and photographic materials for physical development.

Exposure for forming photographic images can be carried out by using various well-known light sources, for example, natural light (sun light), or a tungsten lamp, fluorescent lamp, mercury vapor lamp, xenon arc lamp, carbon arc lamp, xenon flash lamp and cathode ray tube flying spot. The exposure time is usually in a range of 1/1000 to 30 seconds, but can be shorter than 1/1000 second, e.g., in a range of $1/10^4$ to $1/10^6$ second when using a xenon flash lamp or a cathode-ray tube, or longer than 30 seconds. The spectral composition of light to be used for exposure can be controlled with color filters if desired. Laser rays can be used for exposure. In addition, exposure may be conducted by light excited from phosphors by an X-ray, γ-ray or α-ray.

The photographic processing of the photographic materials of the present invention can be carried out by known processes and processing solutions as described, for example, in Research Disclosure No. 176, pp. 28 to 30 (RD-17643). This photographic processing may be carried out for forming silver images (black and white photographic processing) or color images (color photographic processing). The processing temperature is usually in a range of 18 to 50°C, but may be lower than 18°C or higher than 50°C.

The present invention has no limitation with respect to methods of processing color photographic images. Typically, conventional methods include a method of carrying out exposure, color development, bleach-fixing and, if necessary, washing and stabilizing; a method of carrying out exposure, color development, bleaching, fixing, and if necessary, washing and stabilizing; and a method of carrying out exposure, development with a developing solution containing a black and white developing agent, uniform exposure, color development, bleach-fixing and, if necessary, washing and stabilizing; and a method of carrying out exposure, development with a developing solution containing a black and white developing agent, further development with a color developing solution containing a fogging agent (e.g., sodium borohydride), bleach-fixing, and, if necessary, washing and stabilizing.

The aromatic primary amine color developing agents to be used in the color-developing solutions of the present invention include those which are known and widely used in various color photographic processes, for example, amino phenolic and p-phenylenediamine derivatives. Preferably, p-phenylenediamine derivatives are used, and the following are the typical examples thereof, which shall not limit the scope of the present invention.

D-1 N,N-Diethyl-p-phenylenediamine
D-2 2-Amino-5-diethylaminotoluene
D-3 2-Amino-5-(N-ethyl-N-laurylamino)toluene
D-4 4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline
D-5 2-Methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline
D-6 N-Ethyl-N-(β-methanesulfonamide ethyl)-3-methyl-4-aminoaniline
D-7 N-(2-Amino-5-diethylaminophenyl ethyl)methanesulfonamide
D-8 N,N-Dimethyl-p-phenylenediamine

D-9 4-Amino-3-methyl-N-ethyl-N-methoxyethylaniline
D-10 4-Amino-3-methyl-N-ethyl-N-β-ethoxyethylaniline
D-11 4-Amino-3-methyl-N-ethyl-N-β-butoxyethylaniline

Also, these p-phenylenediamine derivatives may be in the form of salts such as a sulfate, hydrochloride, sulfite and p-toluenesulfonate. The above-mentioned compounds are described in U.S. Patents 2,193,015, 2,552,241, 2,566,271, 2,592,364, 3,656,950, and 3,698,525. Thse aromatic primary amine color developing agents are used in an amount of about 0.1 g to about 20 g, preferably about 0.5 g to about 10 g per 1 liter of a developing solution.

The color developing solutions to be used in the present invention can contain hydroxylamines, as is well known.

Hydroxylamines can be used in the form of free amines in the color-developing solutions, but generally are in the form of aqueous solutions of acid salts, such as sulfate, oxalate, chloride, phosphate, carbonate, and acetate thereof. Hydroxylamines may be substituted or unsubstituterd. The nitrogen atoms of hydroxylamines may be substituted with alkyl groups.

Hydroxylamines are added in an amount of preferably 0 to 10 g, more preferably 0 to 5 g, per 1 liter of a color developing solution. As far as the stability of a color developing solution is kept, the smaller amount is better.

As preservatives, there can be added sulfites such as sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metasulfite and potassium metasulfite and carbonyl sulfite additives in an amount of preferably 0 g to 20 g per 1 liter, more preferably 0 g to 5 g per 1 liter. As far as the stability of a color developing solution is kept, the smaller amount is better.

As other preservatives, there are mentioned aromatic polyhydroxy compounds described in JP-A-52-49828, JP-A-56-47038, JP-A-56-32140, JP-A-59-160142, and U.S. Patent 3,746,544; hydroxyacetones described in U.S. Patent 3,615,503 and British Patent 1,306,176; α-aminocarbonyl compounds described in JP-A-52-143020 and JP-A-53-89425; various metals described in JP-A-57-44148 and JP-A-57-53749; various saccharides described in JP-A-52-102727; hydroxamic acids described in JP-A-52-27638; α,α′-dicarbonyl compounds described in JP-A-59-160141; salicylic acids described in JP-A-59-180588; alkanol amines described in JP-A-54-3532; poly(alkyleneimines) described in JP-A-56-94349; and gluconic acid derivatives as described in JP-A-56-75647. Also hydrazine-N,N-diacetic acid is preferred. These pre servatives can be used in a combination of two or more, if desired. Particularly, 4,5-dihydroxy-m-benzenedisulfonic acid, poly(ethylene imine) and triethanol amine are preferably added.

The color developing solutions to be used in the present invention has a pH value of preferably 9 to 12, more preferably 9 to 11, and can contain other compounds known as components of developing solutions.

The detailed description of the kinds and amounts of preservatives, buffers, chelating agents, development accelerators, antifoggants and brightening agents is given in Japanese Patent Application No. 62-63526, pp. 11 to 19.

In the present invention the color developing solution are preferably used at a processing temperature in a range of 20 to 50 °C, preferably 30 to 40 °C, a processing period of time in a range of 20 seconds to 5 minutes, preferably 30 seconds to 4 minutes, and is replenished in an amount of 30 to 1000 ml, preferably 60 to 400 ml per 1 m^2 of a photographic material, though the smaller amount is better.

Desilvering process in the present invention is usually conducted as follows. The desilvering process may generally include any of bleaching step-fixing step; fixing step-bleach-fixing step; bleaching step-bleach- fixing step; and bleach-fixing step. The silvering step is carried out for 2 minutes or less, more preferably for 15 seconds to 90 seconds.

The present invention can employ such bleaching solutions, bleach-fixing solutions, fixing solutions, and additives given to the solutions in the amounts described, for example, in Japanese Patent Application No. 62-63526, pp. 20 to 25.

Also, washing and/or stabilizing after desilvering can be carried out in the same way as described in said Japanese Patent Application No. 62-63526, pp. 25 to 29 line 12.

The present invention is illustrated in greater detail by the following specific Examples, but the invention is not to be construed as being limited thereto. Unless otherwise indicated, all parts, percents and ratios are by weight.

EXAMPLE 1

Specimen (1) for multi-layered color print having the following structure of layers was prepared on a paper support laminated with polyethylene on both sides.

Structure of Layers

The composition of each layer is shown hereinafter. Numerical figures indicate the amounts of coat ings (g/m^2), and the amounts of silver halide emulsions are calculated in terms of silver. However, the amounts of cyan couplers and dyes are given in mol/m^2.

Support

Polyethylene-laminated paper where the polyethylene on the first layer side contained a white pigment (TiO_2) and a blue dye (ultramarine).

The 1st layer (blue-sensitive silver halide emulsion layer)	
Monodisperse silver chlorobromide emulsion containing spectral sensitizer (Sen-1) (EM-1)	0.16
Monodisperse silver chlorobromide emulsion containing spectral sensitizer (Sen-1) (EM-2)	0.10
Antifoggant (Cpd-1)	0.004
Gelatin	1.83
Yellow coupler (ExY)	0.83
Dye image stabilizer (Cpd-2)	0.03
Polymer (Cpd-3)	0.08
Solvents (Solv-1 and Solv-2 in a volume ratio of 1:1)	0.35
Hardening agent (Hd)	0.02

The 2nd layer (color-mixing-preventing layer)	
Gelatin	1.25
Color-mixing-preventing agent (Cpd-4)	0.04
Solvents (Solv-3 and Solv-4 in a volume ratio of 1:1)	0.20
Hardening agent (Hd)	0.02

The 3rd layer (green-sensitive silver halide emulsion layer	
Monodisperse silver chlorobromide emulsion containing spectral sensitizers (Sen-2, 3) (EM-3)	0.05
Monodisperse silver chlorobromide emulsion containing spectral sensitizers (Sen-2, 3) (EM-4)	0.11
Antifoggant (Cpd-5)	0.001
Gelatin	1.79
Magenta coupler (ExM)	0.32
Dye image stabilizer (Cpd-6)	0.20
Dye image stabilizer (Cpd-7)	0.03
Dye image stabilizer (Cpd-8)	0.03
Solvents (Solv-3 and Solv-5 in a volume ratio of 1:2)	0.65
Hardening agent (Hd)	0.01

The 4th layer (ultraviolet absorbing layer)	
Gelatin	1.58
Ultraviolet absorbing agents (UV-1/2/3 in a mol ratio of 1:4:4)	0.62
Color-mixing preventing agent (Cpd-4)	0.05
Solvent (Solv-6)	0.34
Dye (Dy-1)	1.8×10^{-5} (mol/m^2)
Dye (Dy-2)	2.0×10^{-5} (mol/m^2)
Hardening agent (Hd)	0.01

The 5th layer (red-sensitive silver halide emulsion layer)	
Monodisperse silver chlorobromide emulsion (EM-5) containing spectral sensitizers (Sen-4, 5)	0.07
Monodisperse silver chlorobromide emulsion (EM-6) containing spectral sensitizers (Sen-4, 5)	0.15
Antifoggant (Cpd-9)	0.0002
Gelatin	1.34
Cyan coupler in Table 2	6.7×10^{-4} (mol/m^2)
Ultraviolet absorbing agents (UV-1/3/4 in a mol ratio of 1:3:3)	0.17
Polymer (Cpd-3)	0.33
Solvent (Solv-1)	0.23
Hardening agent (Hd)	0.01

The 6th layer (ultraviolet absorbing layer)	
Gelatin	0.53
Ultraviolet absorbing agents (UV-1/2/3 in a mol ratio of 1:4:4)	0.21
Solvent (Solv-6)	0.08
Hardening agent (Hd)	0.01

The 7th layer (protective layer)	
Gelatin	1.33
Acryl-denatured copolymer of polyvinyl alcohol (denaturation degree: 17%)	0.17
Liquid paraffin	0.03

The silver halide emulsion (EM-1) used in the above specimen was prepared as follows:

(Solution 1)

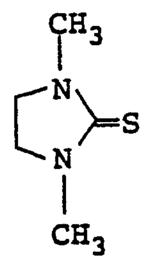
H_2O	1000 ml
NaCl	5.5 g
Gelatin	25 g

(Solution 2)

Sulfuric acid (1N)	20 ml

(Solution 3)

A compound of the following formula (1% aqueous solution)	2 ml



(Solution 4)

KBr	2.80 g
NaCl	0.34 g

H_2O was added to equal to 140 ml.

(Solution 5)

$AgNO_3$	5 g

H_2O was added to equal to 140 ml.

(Solution 6)

KBr	67.20 g

NaCl	8.26 g
K_2IrCl_6 (0.001% aqueous solution)	0.7 ml
H_2O was added to equal to 320 ml.	

(Solution 7)

$AgNO_3$	120 g
NH_4NO_3 (50% aqueous solution)	2 ml
H_2O was added to equal to 320 ml.	

Solution 1 was heated to 74°C, to which solutions 2 and 3 were added. Then, solutions 4 and 5 were added thereto at the same time in 9 minutes. Further 10 minutes after, solutions 6 and 7 were added at the same time in 45 minutes. Then the mixed solution was allowed to stand for 5 minutes after the addition thereof, and then cooled and desalted. Water and dispersion gelatin were added to adjust the pH to 6.2, to obtain a monodisperse cubic silver chlorobromide emulsion having an average particle size of 0.96 µm, a coefficient of variation (a value obtained by dividing standard deviation by an average particle size: $s/\overline{d}$) of 0.08, and 80 mol% of silver bromide. This emulsion was optimumly chemically sensitized with sodium thiosulfate.

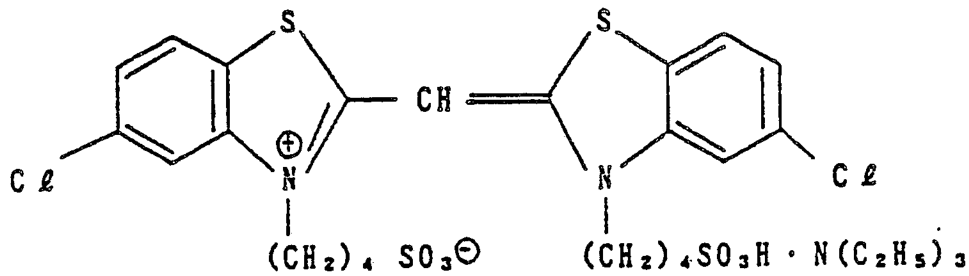
The other silver chlorobromide emulsions (EM-2) to (EM-6) were prepared in a manner similar to the above emulsion (EM-1) except for changing the amounts of chemicals, temperature and time.

The following Table 1 shows the details of these emulsions.

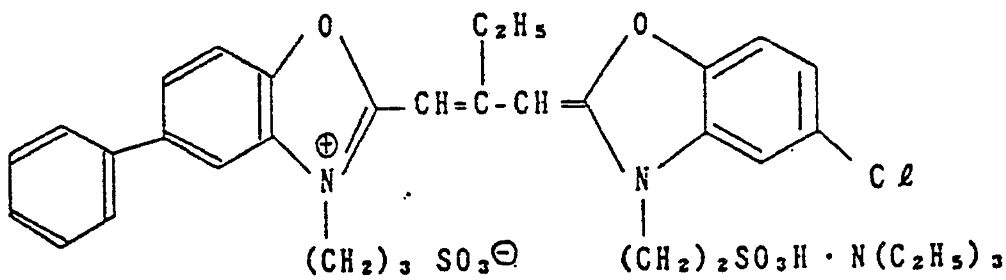
TABLE 1

Emulsion nameù	Form	Average particle size (µm)	Br content (mol%)	Coefficient of variation
EM-1	Cube	0.96	80	0.08
EM-2	"	0.64	80	0.07
EM-3	"	0.52	95	0.08
EM-4	"	0.40	95	0.09
EM-5	"	0.44	70	0.09
EM-6	"	0.36	70	0.08
Coefficient of variation = standard deviation/average particle size				

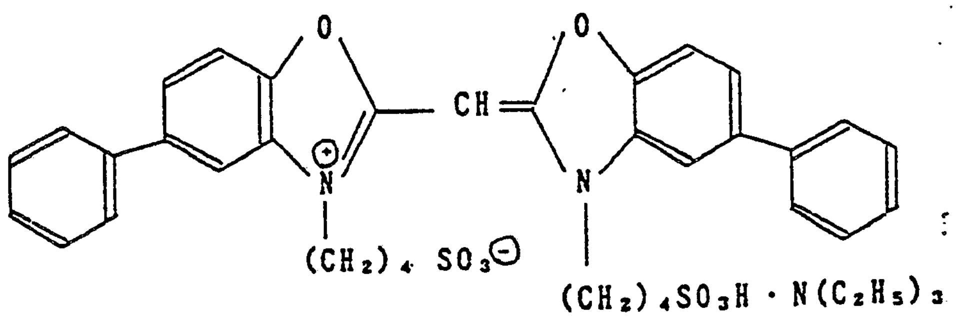
(Sen-1) 6×10^{-4} mol / A g-mol



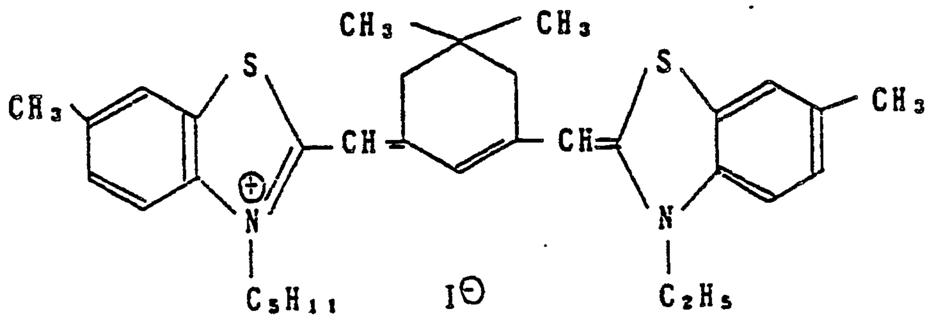
(Sen-2) 4×10^{-4} mol / A g-mol



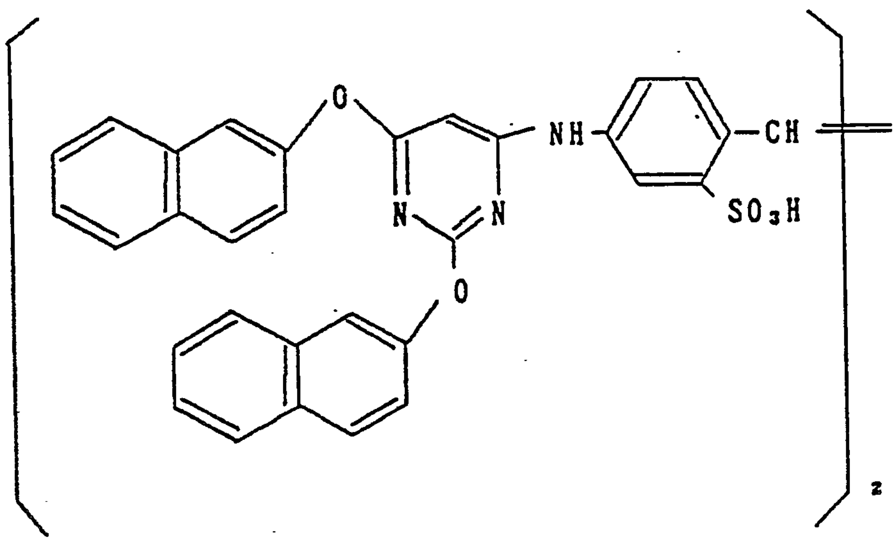
(Sen-3) 8×10^{-5} mol / A g-mol



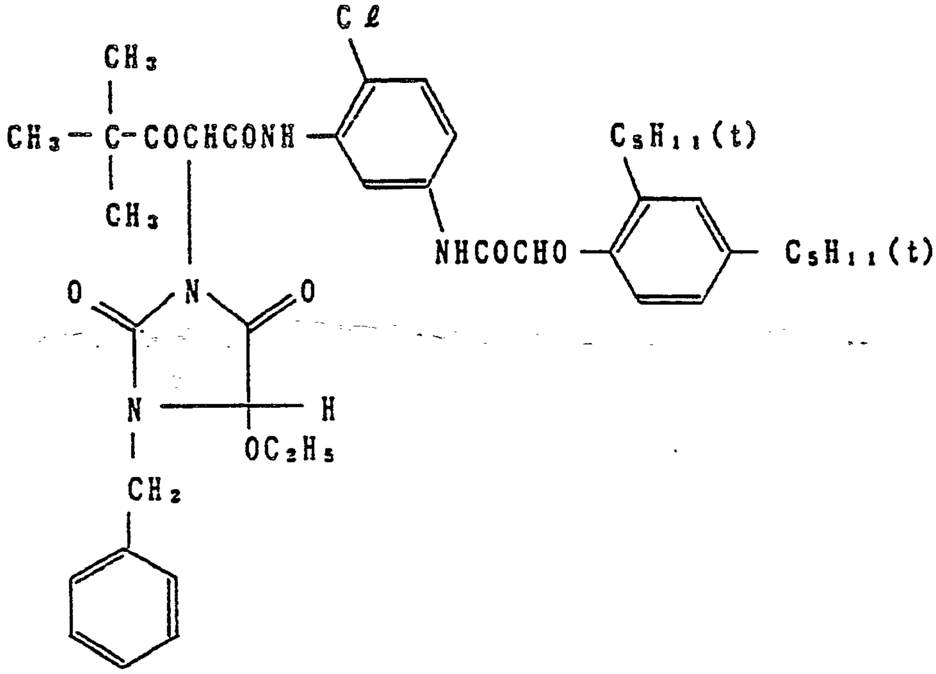
(Sen-4) 1.8×10^{-4} mol/A g-mol



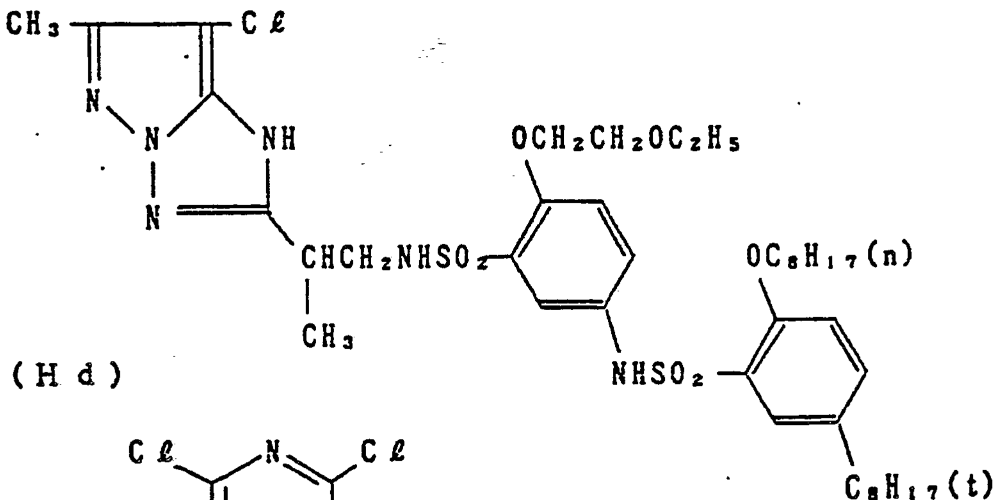
(Sen-5) 3×10^{-3} mol/A g-mol



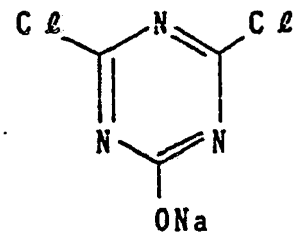
(ExY)



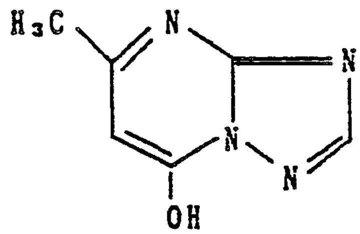
(ExM)



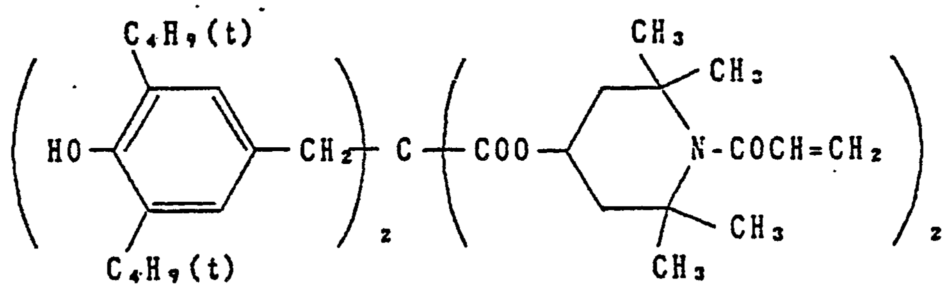
(Hd)



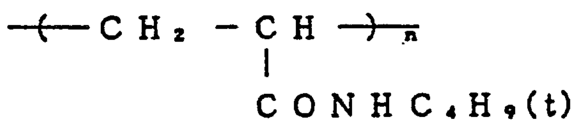
(Cpd-1)



(Cpd-2)

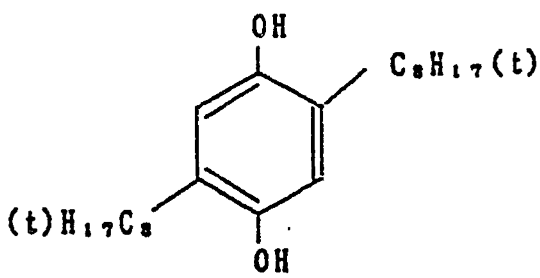


(Cpd-3)

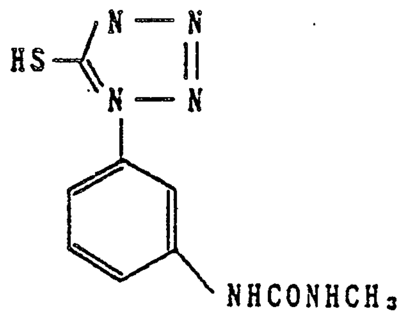


Molecular weight: about 60,000

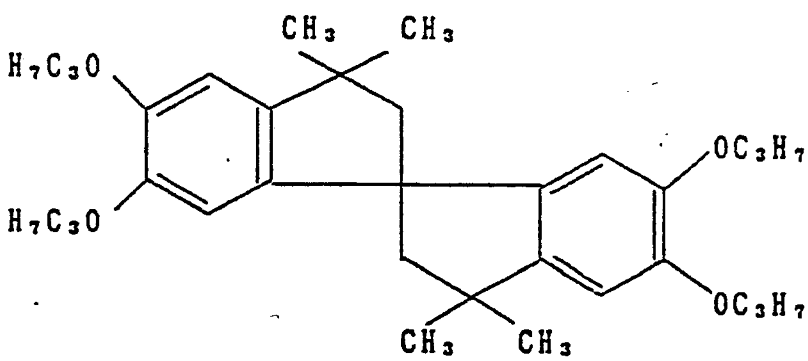
(Cpd-4)



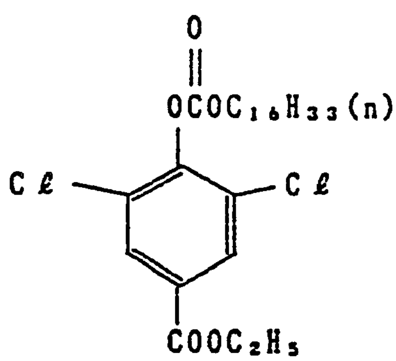
(Cpd-5)



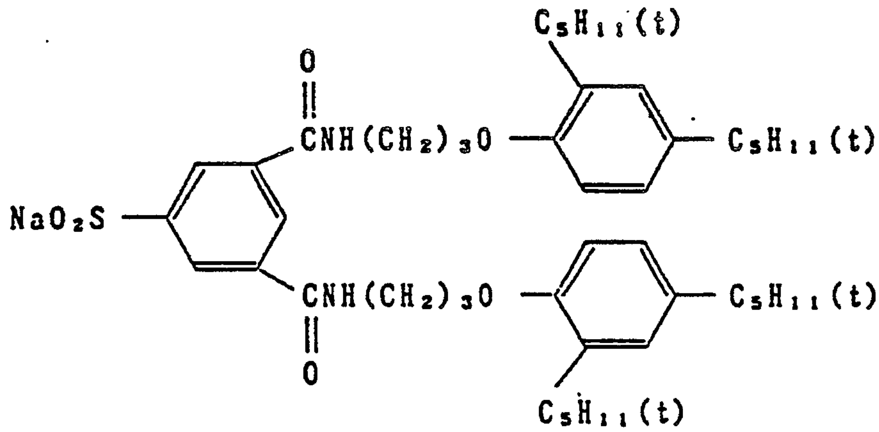
(Cpd-6)



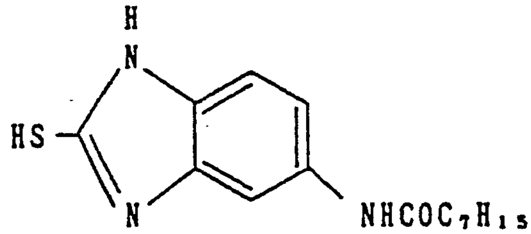
(Cpd-7)



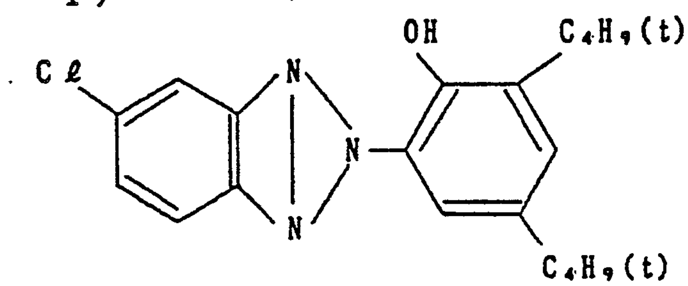
(Cpd-8)



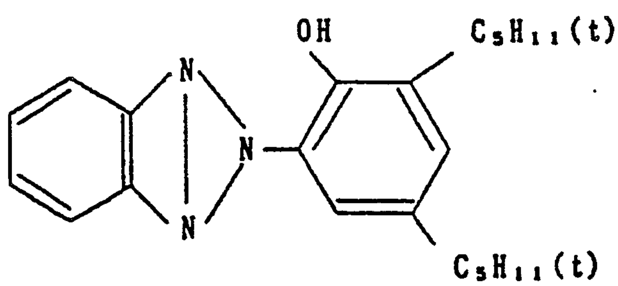
(Cpd-9)



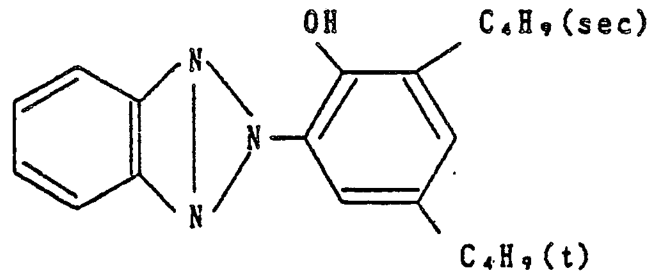
(UV-1)



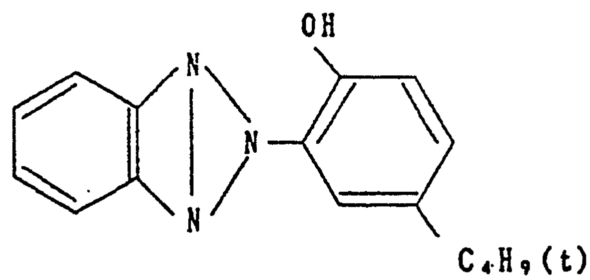
(UV-2)



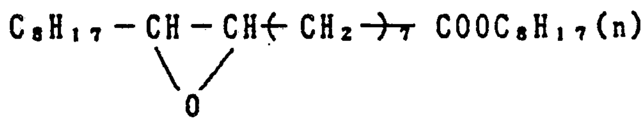
(UV-3)



(UV-4)



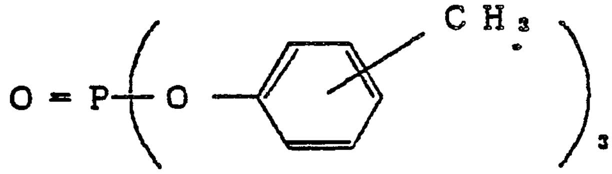
(Solv-1)



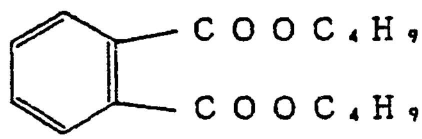
(Solv-2)

$$O=P\leftarrow OC_9H_{19}(iso))_3$$

(Solv-3)



(Solv-4)



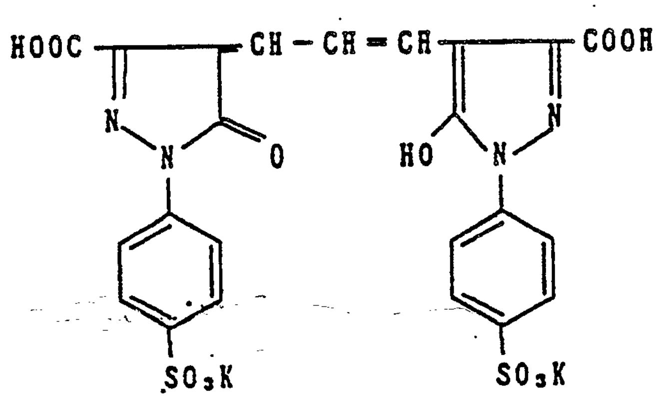
(Solv-5)

$$O=P\left(OCH_2\underset{}{\overset{C_2H_5}{\overset{|}{C}}}HC_4H_9\right)_3$$

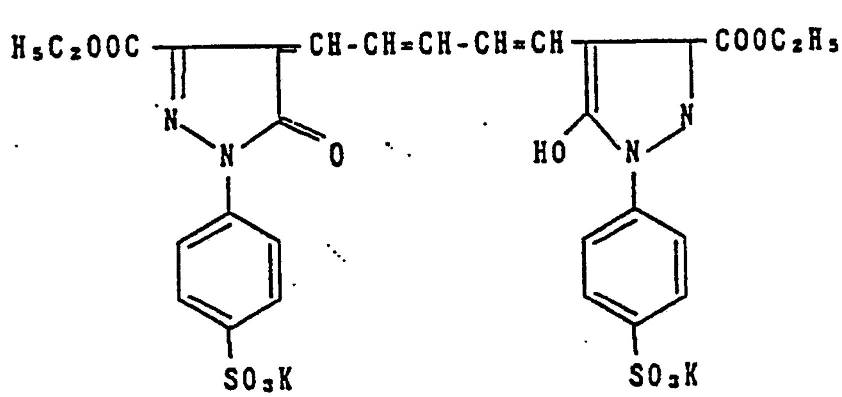
(Solv-6)

$$\begin{array}{l} COOCH_2CH(C_2H_5)C_4H_9 \\ | \\ (CH_2)_8 \\ | \\ COOCH_2CH(C_2H_5)C_4H_9 \end{array}$$

(D y - 1)



(D y - 2)



Specimens (2) to (7) were prepared in the same manner as the above specimen (1) except for changing the dyes of the 4th layer and the cyan coupler of the 5th layer. The compositions of dyes and cyan couplers were shown in Table 2. It is to be noted that the numbers of dyes and cyan couplers correspond to those given in Examples. The following cyan coupler (C) was used for comparison.

Cyan coupler (C)

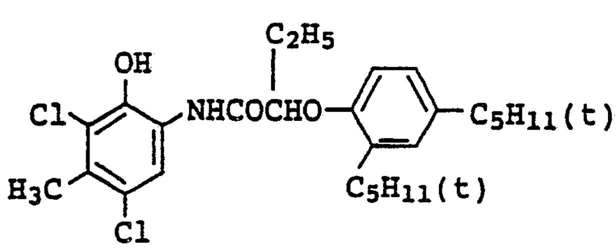


TABLE 2

Specimen	Dye (amount used: mol/m²)	Cyan coupler (6.7×10^{-4} mol/m²)	
(1)	Dy-1 (1.8×10^{-5}) Dy-2 (1.8×10^{-5})	(C)	Control
(2)	"	C-3	"
(3)	I-37 (1.8×10^{-5}) I-10 (2.0×10^{-5})	(C)	"
(4)	"	C-3	Present Invention
(5)	"	C-1	"
(6)	"	C-2, C-3 (mol ratio of 1:1)	"
(7)	I-5 (1.8×10^{-5}) I-8 (2.0×10^{-5})	C-3	"

Gradation exposure for sensitometry was given to specimens (1) to (7) through a red filter using a sensitometer (FWH type made by Fuji Photo Film Co., Ltd., color temperature of light source: 3200K). In this regard, exposure was carried out for 0.1 second to obtain exposure of 250 CMS. As to sharpness, exposure was given through optical wedge for sharpness to obtain a cyan density of 1.5.

After exposure, the following steps of color development, bleach-fixing, and washing were carried out.

Processing Step	Temperature (°C)	Time
Color development	33	3 min. 30 sec.
Bleach-fixing	33	1 min. 30 sec.
Washing	24 to 34	3 min.
Drying	70 to 80	1 min.

The composition of each processing solution was given as follows:

Color developing solution	
Water	800 ml
Diethylenetriaminepentaacetic acid	1.0 g
Nitrilotriacetic acid	1.5 g
Benzyl alcohol	15 ml
Diethylene glycol	10 ml
Sodium sulfite	2.0 g
Potassium bromide	0.5 g
Potassium carbonate	30 g
N-ethyl-N-(β-methane sulfonamide ethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
Hydroxylamine sulfate	4.0 g
Brightening agent (WHITEX 4B, made by Sumitomo Chemical Co., Ltd.)	1.0 g
Water was added to equal to 1000 ml.	
pH (25°C)	10.20

Bleach-fix bath	
Water	400 ml
Ammonium thiosulfate (70% aqueous solution)	150 ml
Sodium sulfite	18 g
Iron(III) ammonium ethylenediamine tetraacetate	55 g
Disodium ethylenediaminetetraacetate	5 g
Water was added to equal to 1000 ml.	
pH (25 °C)	6.70

The above specimens (1) to (7) were developed and then evaluated as to sensitivity, fogging, sharpness and discoloration. In this regard, the values of relative sensitivity in a density of 1.0 were obtained with using the relative sensitivity value of specimen (1) of 100 for convenience; the values of fogging were obtained in the developing times of 3 minutes 30 second and also in the forced development time of 7 minutes; and the values of sharpness were obtained by determining C.T.F. (contrast transfer function) (%) in a spatial frequency of 15 cycles/mm, in which the higher value of sharpness was better. Further, the values of dark discoloration were obtained by leaving each of the developed specimens at 80 °C in 70% RH for 14 days and evaluating the percentage of the density obtained in 14 days as to the portion having the color density of 2.0 obtained before the test. The results are shown in Table 3.

TABLE 3

Specimen	Sensitivity	Value of fog		Sharpness	Dark discoloration	
		3.5 min.	7 min.			
(1)	100	0.09	0.12	29.5	74	Control
(2)	91	0.09	0.13	29.3	87	"
(3)	107	0.08	0.09	33.2	76	"
(4)	120	0.08	0.09	34.0	89	Present Invention
(5)	117	0.08	0.09	33.9	92	"
(6)	120	0.08	0.09	33.9	88	"
(7)	115	0.08	0.09	33.8	89	"

As clearly shown in Table 3, the specimens of the present invention prepared by combining cyan couplers and dyes are good photographic materials having high sensitivity, less fogging, high sharpness and good resistance to dark discoloration.

EXAMPLE 3

Specimen (8) having the following composition was prepared in the same manner as Example 1.

The 1st layer (blue-sensitive silver halide emulsion layer)	
Monodisperse silver chlorobromide emulsion containing spectral sensitizer (Sen-6) (EM-7)	0.27
Gelatin	1.86
Yellow coupler (ExY)	0.82
Solvent (Solv-4)	0.35
Hardening agent (Hd)	0.02

The 2nd layer (color-mixing-preventing layer)	
Gelatin	0.99
Color-mixing-preventing agent (Cpd-4)	0.06
Solvents (Solv-3 and Solv-4 in a volume ratio of 1:1)	0.12
Hardening agent (Hd)	0.02

The 3rd layer (green-sensitive silver halide emulsion layer)	
Monodisperse silver chlorobromide emulsion containing spectral sensitizers (Sen-7, 3) (EM-8)	0.45
Gelatin	1.24
Magenta coupler (ExM)	0.35
Dye image stabilizer (Cpd-6)	0.20
Dye image stabilizer (Cpd-7)	0.03
Dye image stabilizer (Cpd-8)	0.03
Solvents (Solv-3 and Solv-5 in a volume ratio of 1:2)	0.65
Hardening agent (Hd)	0.01

The 4th layer (ultraviolet absorbing layer)	
Gelatin	1.58
Ultraviolet absorbing agent (UV-1/2/3 in a mol ratio of 1:4:4)	0.62
Color-mixing-preventing agent (Cpd-4)	0.05
Solvent (Solv-6)	0.34
Dye (Dy-1)	1.8×10^{-5} (mol/m^2)
Dye (Dy-2)	2.0×10^{-5} (mol/m^2)
Hardening agent (Hd)	0.01

The 5th layer (red-sensitive silver halide emulsion layer)	
Monodisperse silver chlorobromide emulsion containing spectral sensitizers (Sen-4, 5) (EM-9)	0.20
Gelatin	0.92
Cyan coupler (Table 5)	6.7×10^{-4} (mol/m^2)
Polymer (Cpd-3)	0.30
Ultraviolet absorbing agent (UV-1/3/4 in a mol ratio of 1:3:3)	0.17
Solvent (Solv-4)	0.20
Hardening agent (Hd)	0.01

The 6th layer (ultraviolet absorbing layer)	
Gelatin	0.53
Ultraviolet absorbing agent (UV-1/2/3 in a mol ratio of 1:4:4)	0.21
Solvent (Solv-6)	0.08
Hardening agent (Hd)	0.01

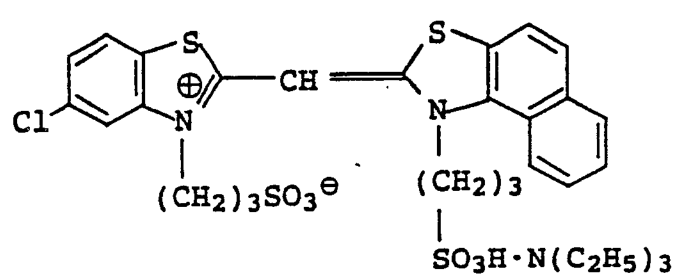
The 7th layer (protective layer)	
Gelatin	1.33
Acryl-denatured copolymer of polyvinyl alcohol (denaturation degree 17%)	0.17
Liquid paraffin	0.03

The details of the particles of AgBrCl in the silver halide emulsions used in the above-mentioned specimens are shown in Table 4.

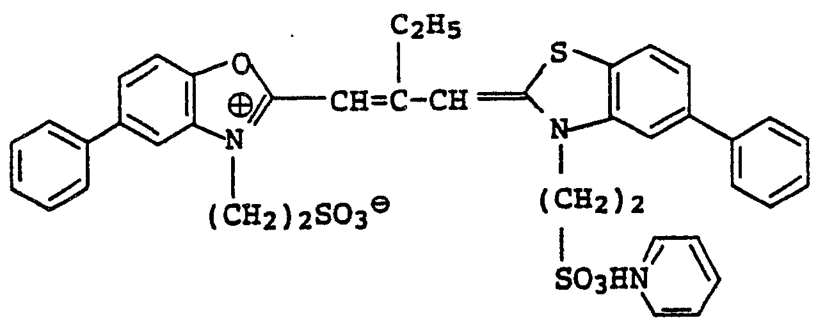
TABLE 4

Emulsion	Form	Average particle diameter	Br content	Coefficient of variation
		(μm)	(mol%)	
EM-7	Cube	0.85	0.6	0.10
EM-8	"	0.45	1.0	0.09
EM-9	"	0.34	1.8	0.10
Coefficient of variation = Standard deviation/average particle diameter				

(Sen-6)



(Sen-7)



Specimens (8) to (12) were prepared by changing the dyes of the 4th layer and the cyan couplers of the 5th layer in the above specimen. The compositions thereof were shown in Table 5.

TABLE 5

Specimen	Dye	Cyan coupler	
	(Amount: mol/m^2)	(6.7×10^{-4} mol/m^2)	
(8)	Dy-1 (1.8×10^{-5}) Dy-2 (2.0×10^{-5})	(C)	Control
(9)	"	C-1	"
(10)	I-37 (1.8×10^{-5}) I-10 (2.0×10^{-5})	(C)	"
(11)	"	C-1	Present Invention
(12)	"	(C), C-14 (mol ratio of 1:1)	"

The specimens (8) to (12) were exposed to light and treated by the following steps to obtain the evaluation thereof the same as Example 1.

Processing Step	Temperature (°C)	Time
Color development	35	45 sec.
Bleach-fixing	30 to 35	45 sec.
Rinse (1)	30 to 35	20 sec.
Rinse (2)	30 to 35	20 sec.
Rinse (3)	30 to 35	20 sec.
Rinse (4)	30 to 35	30 sec.
Dry	70 to 80	60 sec.
(A 3-tank countercurrent system of rinse (4)→(1) was employed).		

The composition of each processing solution is given as follows:

Color-developing solution	
Water	800 ml
Ethylene diamine-N,N,N′,N′-tetramethylene phosphonic acid	1.5 g
Triethylene diamine (1,4-diazabicyclo(2,2,2)octane)	5.0 g
Sodium chloride	1.4 g
Potassium carbonate	25 g
N-Ethyl-N-(β-methanesulfonamide ethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
N,N-Diethylhydroxylamine	4.2 g
Brightening agent (UVITEX CK made by Ciba Geigy Co., Ltd.)	2.0 g
Water was added to equal to	1000 ml
pH (25°C)	10.10

Bleach-fixing bath	
Water	400 ml
Ammonium thiosulfate (70%)	100 ml
Sodium sulfite	18 g
Iron(III) ammonium ethylene diamine tetraacetate	55 g
Disodium ethylene diamine tetraacetate	3 g
Ammonium bromide	40 g
Glacial acetic acid	8 g
Water was added to equal to	1000 ml
pH (25 °C)	5.5

Rinsing bath
Ion exchange water (each of calcium and magnesium in 3 ppm or less).

The specimens (8) to (12) were developed and evaluated in the same manner as Example 1, with the sensitivity values were obtained when the relative sensitivity of specimen (8) was considered as 100, and the values of fog formed by forced development were obtained when the development time was 90 seconds. The results are shown in Table 6.

TABLE 6

Specimen	Sensitivity	Value of fog		Sharpness	Dark discoloration	
		3.5 min.	7 min.			
(8)	100	0.09	0.12	29.0	75	Control
(9)	87	0.09	0.13	28.9	88	"
(10)	107	0.08	0.09	33.0	75	"
(11)	123	0.08	0.09	34.0	92	Present Invention
(12)	120	0.08	0.09	33.8	90	"

As clearly shown in Table 6, the specimens containing the combinations of cyan couplers and dyes are good photographic materials which have high sensitivity, low fogging values, high sharpness and good resistance to dark discoloration.

EXAMPLE 3

In order to examine the stability of the dyes of the present invention in the films, the specimens (2), (4), (7), (9) and (11) of Examples 1 and 2 were allowed to stand at 35 °C and 80% R.H. for 2 weeks and then evaluated to determine the percentages of the remaining dyes. The results are shown in Table 7.

TABLE 7

Specimen	Percentage of remaining dyes	
	(%)	
(2)	80	Control
(4)	95	Present Invention
(7)	92	Present Invention
(9)	82	Control
(11)	95	Present Invention

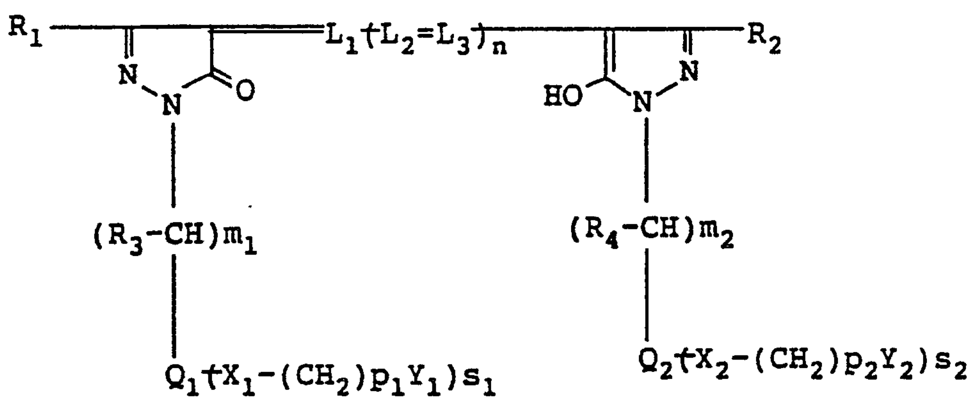
The result reveals that the dyes of the present invention have good stability in films.

The present invention can provide silver halide color photographic materials having hydrophilic colloidal layers containing new dyes which are easily decolored by processing and are stable even after the lapse of time without exerting any harmful effect on the photographic properties of photographic emulsions, particularly on sensitivity and fog. Moreover, the present invention can provide silver halide color photographic materials including a red-sensitive emulsion layer which has good resistance to dark discoloration, high sharpness, high sensitivity and low fog.

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 photographic material which comprises a support having at least one silver halide color photographic emulsion layer coated thereon and containing at least one compound represented by the following general formula (I) and at least one compound represented by the following general formula (II) in at least one of hydrophilic layers provided on the support:



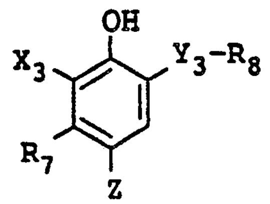
(I)

wherein each of R_1 and R_2 represents $-COOR_5$ or

$$-CON\begin{matrix} R_5 \\ R_6 \end{matrix} \quad ;$$

each of R_3 and R_4 represents hydrogen or an alkyl group; each of R_5 and R_6 represents a hydrogen atom, an unsubstituted alkyl group, an aryl group or R_5 and R_6 together form a 5- or 6-membered ring; each of Q_1 and Q_2 represents an aryl group; each of X_1 and X_2 represents a divalent bonding group or a bond;

each of Y_1 and Y_2 represents a sulfonic acid group or a carboxylic acid group; each of L_1, L_2 and L_3 represents a methine group; each of m_1 and m_2 represents 1 or 2; n represents 0, 1 or 2; each of p_1 and p_2 represents 0, 1, 2, 3 or 4; and each of s_1 and s_2 represents 1 or 2; and



(II)

wherein Y_3 represents -NHCO- or -CONH-; R_8 represents an aliphatic group, an aromatic group, a heterocyclic group or an aryl amino group which may be substituted; X_3 represents hydrogen, a halogen atom, an alkoxy group or an acylamino group; R_7 represents an alkyl group (containing two or more carbon atoms), an acyl amino group or a nonmetallic atomic group necesasry to form a 5 to 7 membered ring by the combination of X_3 and R_7; and Z represents a hydrogen atom or a group which can be released by coupling with an oxidized color developing agent.

2. A silver halide color photographic material as in claim 1, wherein said compound represented by formula (I) is used in such an amount that the compound provide optical density of 0.05 to 3.0.

3. A silver halide color photographic material as in claim 1, wherein said compound represented by formula (I) is incorporated in at least one of hydrophilic colloidal layers.

4. A silver halide color photographic material as in claim 1, wherein the amount of said compound represented by formula (II) is 0.1 to 1 mol per mol of silver halide in the photographic silver halide emulsion layer containing the compound.

5. A silver halide color photographic material as in claim 1, wherein the alkyl group represented by R_5 or R_6 is substituted with a substituent selected from the group consisting of a sulfo group, a carboxyl group, a hydroxy group, an alkoxy group, a halogen atom, a cyano group, an aliphatic or aromatic-sulfonyl group, a nitro group, an amino group unsubstituted or substituted with an alkyl group, and an aryl group.

6. A silver halide color photographic material as in claim 1, wherein the aryl group represented by R_5 or R_6 is a phenyl group unsubstituted or substituted with a substituent selected from the group consisting of a sulfo group, a carboxyl group, a hydroxy group, an alkoxy group, a halogen atom, a cyano group, a nitro group, an amino group unsubstituted or substituted with an alkyl group, and an alkyl group.

7. A silver halide color photographic material as in claim 1, wherein R_1 and R_2 each forms sodium salt, potassium salt, ammonium salt or tetraammonium salt.

8. A silver halide color photographic material as in claim 1, wherein the aryl group represented by Q_1 or Q_2 represents 2- or 3-valent phenyl or naphthyl group or a phenyl group substituted with a substituent selected from the group consisting of a C_1 to C_4 alkyl group, a C_1 to C_4 alkoxy group a halogen atom, an aliphatic or aromatic carbamoyl group, an aliphatic or aromatic sulfamoyl group, a cyano group, a nitro group, an alkylsulfonyl group, an arylsulfonyl group, an amino group unsubstituted or substituted with an alkyl group, an aliphatic or aromatic acylamino group, and an aliphatic or aromatic sulfonamido group.

9. A silver halide color photographic material as in claim 1, wherein X_1 and X_2 each represents

$$-O-,\ -\overset{\displaystyle R_7}{\overset{|}{N}}-,\ -\overset{\displaystyle R_7}{\overset{|}{N}}-CO-,\ -SO_2,\ -\overset{\displaystyle R_7}{\overset{|}{N}}-SO_2,$$

or a bond, wherein R_7 represents hydrogen, a C_1 to C_5 alkyl group, or a C_1 to C_5 (total) substituted alkyl group having a substituent selected from the group consisting of a C_1 to C_3 alkoxy group, a sulfo group, a carboxyl group, a cyano group, a hydroxy group, an amino group unsubstituted or substituted with an alkyl group, an aliphatic or aromatic sulfonamido group, an aliphatic or aromatic carbonamido group, an aliphatic or aromatic carbamoyl group, and an aliphatic or aromatic sulfamoyl group.

10. A silver halide color photographic material as in claim 1, wherein Y_1 and Y_2 each represents a sulfonic acid group or a carboxylic acid group which may form a free acid or a salt.

11. A silver halide color photographic material as in claim 1, wherein L_1, L_2 and L_3 each represents a methyne group or a methyne group substituted with a substituent selected from the gorup consisting of a methyl group, an ethyl group, and a phenyl group.