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(54) Positive working silver halide color photographic material.

(57) A positive working silver halide color photographic material which comprises a support having thereon at least one silver halide emulsion layer, wherein the photographic material contains (a) at least one dye having a maximum absorption wavelength of 480 to 530 nm in a gelatin film and/or (b) at least one dye having a maximum absorption wavelength of 580 to 630 nm in a gelatin film with the proviso that an oxonol dye having a hydroxypyridone nucleus is excluded when a dye (a) or a dye (b) is present alone.

POSITIVE WORKING SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

This invention relates to a positive working silver halide color photographic material and, more particularly, to a positive working silver halide color photographic material having improved color reproducibility. The term "positive working silver halide color photographic materials" as used herein means those materials which can produce reflex, semi-transmission or transmission type positive images (copies) using reflex or transmission type positive images (originals).

BACKGROUND OF THE INVENTION

Photographic emulsion layers or other layers in silver halide photographic materials are often colored so that light in specific wave ranges is absorbed.

A colored layer is provided farther from support than the photographic emulsion in the photographic materials when it is necessary to control the spectral composition of incident light on the photographic emulsion layers. Such a colored layer is called a filter layer. When a plurality of photographic layers are provided as in multilayer color photographic materials, the filter layer is interposed therebetween.

A colored layer is often provided between a photographic emulsion layer and a support or on the opposite side of the support to the photographic emulsion for the purpose of preventing image blurring, that is, preventing "halation" from occurring, this blurring or halation being caused by the fact that light which is scattered during or after passage through the photographic emulsion is reflected at the interface between the emulsion layer and the support or on the opposite side of the photographic material to the emulsion layer and again enters the emulsion layer. Such a colored layer is called an antihalation layer. When a multilayer color photographic material is used, the antihalation layer is often interposed between the layers.

Photographic emulsion layers are often colored to prevent image sharpness from being reduced by the scattering of light in the photographic emulsion (this phenomenon is generally called "irradiation").

Many of these layers to be colored comprise hydrophilic colloid layers and hence water-soluble dyes are generally incorporated in these layers to color them. The dyes must meet the following requirements.

(1) The dyes must have proper spectral absorption according to their purpose.

(2) The dyes must be photographically chemically inactive. Namely, they must not chemically adversely affect the performance of the silver halide photographic emulsions. For example, they must not cause a lowering of sensitivity, a fading of the latent image or fogging.

(3) The dyes must be decolorized or removed by dissolution during the course of photographic processing so that a harmful color does not remain in the photographic material after processing.

Efforts have been made by those skilled in the art to find dyes which meet these requirements. There are known dyes such as oxonol dyes having a pyrazolone nucleus or a barbituric acid nucleus as 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-48-85130, JP-A-49-114420, JP-A-52-20830, JP-A-55-161233, JP-A-59-111640 (the term "JP-A" as used herein refers to a "published unexamined Japanese patent application"), U.S. Patents 3,247,127, 3,469,985, 3,746,539 and 4,078,933; oxonol dyes as described in U.S. Patents 2,533,472 and 3,379,533, British Patent 1,278,621 and West German Patent 2,928,184; azo dyes as described in British Patents 575,691, 680, 631, 599,623, 780,907, 907,125 and 1,045,609, U.S. Patent 4,255,326 and JP-A-59-211043; azomethine dyes as described in JP-A-50-100116, JP-A-54-118247, British Patents 2,014,598 and 750,031; anthraquinone dyes as described in U.S. Patent 2,865,752; arylidene dyes as described in U.S. Patents 2,538,009, 2,688,541 and 2,538,008, British Patents 58,609 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-B-59-37303 (the term "JP-B" as used herein refers to an "examined Japanese patent publication"); styryl dyes as described in JP-B-28-3082, JP-B-44-16594 and JP-B-59-28898; triarylmethane dyes as described in British Patents 446,583 and 1,335,422 and JP-A-59-228250; merocyanine dyes as described in British Patents 1,075,653, 1,153,341, 1,284,730, 1,475,228 and 1,542,807; and cyanine dyes as described in U.S. Patents 2,842,486 and 3,294,539.

Of these, the oxonol dyes having two pyrazolone nuclei have properties such that they are decolorized in developing solutions containing sulfites and have little adverse effects on the photographic emulsions. Therefore, they have been used as useful dyes for the photographic materials.

Of these, however, there are dyes which have the disadvantages that dyes which are spectrally sensitized in undesired regions are formed when subjected to spectral sensitization, or a reduction in sensitivity occurs apparently by the desorption of sensitizing dyes, although they have little adverse effects on the photographic emulsions.

Some dyes remain after processing in rapid development which has been conducted recently. To solve this problem, use of dyes which are highly reactive with sulfite ions has been proposed. However, there are disadvantages in that these dyes have poor stability in photographic emulsion films, a reduction in density occurs with the passage of time and desired photographic effects cannot be obtained.

Further, the use of specific oxonol dyes have been proposed in JP-A-52-20830, U.S. Patent 3,746,539 and West German Patent 2,928,184 to improve color reproducibility in color photographic materials or to enhance safelight stability. However, use of these dyes has the disadvantage that, in addition to the above-described problems, the spectral absorption of the dyes is improper so that when a large amount thereof is added to obtain a sufficient effect, photographic sensitivity is reduced.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a positive working color photographic material which has improved color reproducibility and is scarcely colored by dye remaining after processing.

The above-described object of the present invention is achieved by a positive working silver halide color photographic material comprising a support having thereon at least one silver halide emulsion layer wherein the photographic material contains (a) at least one dye having a maximum absorption wavelength of 480 to 530 nm in a gelatin film and/or (b) at least one dye having a maximum absorption wavelength of 580 to 630 nm in a gelatin film, with the proviso that an oxonol dye having a hydroxypyridone nucleus is excluded when only a dye (a) or a dye (b) is present in the photographic material.

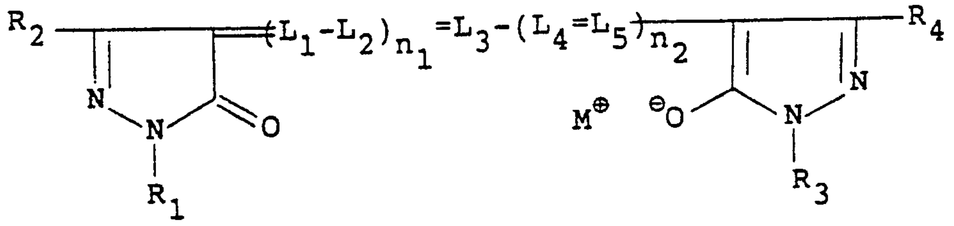
Thus, the silver halide color photographic material of the present invention contains (a) at least one dye having a maximum absorption wavelength of 480 to 530 nm in a gelatin film and/or (b) at least one dye having a maximum absorption wavelength of 580 to 630 nm in a gelatin film.

With regard to the dyes (a) having a maximum absorption wavelength of 480 to 530 nm in a gelatin film, the half width of absorption is 90 nm or above and with regard to the dyes (b) having a maximum absorption wavelength of 580 to 630 nm in a gelatin film, the half width of absorption is 100 nm or below.

DETAILED DESCRIPTION OF THE INVENTION

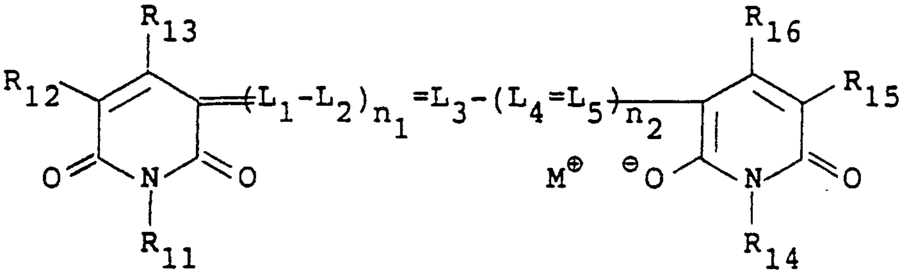
The present invention is illustrated in more detail below.

Of the dyes (a) having a maximum absorption wavelength of 480 to 530 nm in a gelatin film and the dyes (b) having a maximum absorption wavelength of 580 to 630 nm in a gelatin film, oxonol dyes having a pyrazolone nucleus, oxonol dyes having a hydroxypyridone nucleus, oxonol dyes having a barbituric acid nucleus, and oxonol dyes having a pyrazolidinedione nucleus are preferred and compounds represented by the following general formula (I), (Ia), (II), (IIa), (III) or (IV) are particularly preferred.

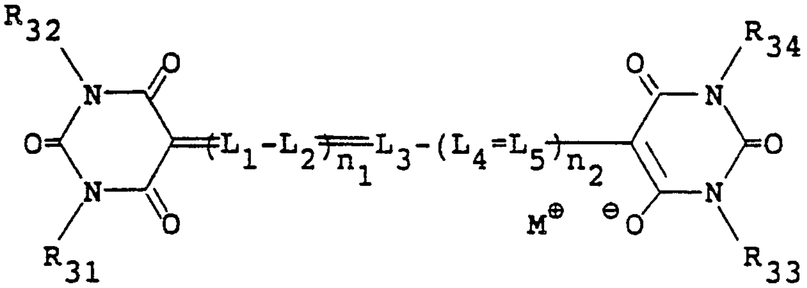


(I)

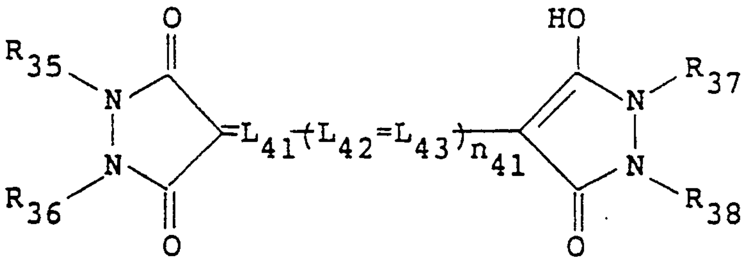
wherein R_1 and R_3, which may be the same or different, each represents an aliphatic group, an aromatic group or a heterocyclic ring; R_2 and R_4, which may be the same or different, each represents an aliphatic group, an aromatic group, $-OR_5$, $-COOR_5$, $-NR_5R_6$, $-CONR_5R_6$, $-NR_5CONR_5R_6$, $-SO_2R_7$, $-COR_7$, $-NR_6COR_7$, $-NR_6SO_2R_7$, or a cyano group, wherein R_5 and R_6, which may be the same or different, each represents a hydrogen atom, an aliphatic group or an aromatic group; R_7 represents an aliphatic group or an aromatic group; and R_5 and R_6 or R_6 and R_7 may combine together to form a 5-membered or 6-membered ring; n_1 and n_2 each represents 0 or 1; $M^\oplus$ represents a hydrogen atom or a monovalent cation; L_1, L_2, L_3, L_4 and L_5 each represents a methine group.


(II)

wherein R_{11} and R_{14}, which may be the same or different, each represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, $-NR_{17}R_{18}$, $-NR_{17}CONR_{17}R_{18}$, $-NR_{18}COR_{19}$, or $-NR_{18}SO_2R_{19}$; R_{12} and R_{15}, which may be the same or different, each represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a sulfo group, $-NR_{17}R_{18}$, $-NR_{18}COR_{19}$, $-NR_{18}SO_2R_{19}$, $-NR_{17}CONR_{17}R_{18}$, $-COOR_{17}$, $-CONR_{17}R_{18}$, $-COR_{19}$, $-SO_2R_{19}$ or $-SO_2NR_{17}R_{18}$; R_{13} and R_{16}, which may be the same or different, each represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, $-OR_{17}$, $-COOR_{17}$, $-COR_{19}$, $-CONR_{17}R_{18}$, $-NR_{17}R_{18}$, $-NR_{18}COR_{19}$ or $-NR_{18}SO_2R_{19}$, $-NR_{17}COR_{17}R_{18}$, $-SO_2R_{19}$, $-SO_2NR_{17}R_{18}$, $-OR_7$ or a cyano group, wherein R_{17} and R_{18}, which may be the same or different, each represents a hydrogen atom, an aliphatic group or an aromatic group; R_{19} is an aliphatic group or an aromatic group; R_{17} and R_{18} or R_{18} and R_{19} may combine together to form a 5-membered or 6-membered ring; and L_1, L_2, L_3, L_4, L_5, n_1, n_2 and $M^\oplus$ are as defined above in the formula (I).


(III)

wherein R_{31}, R_{32}, R_{33} and R_{34}, which may be the same or different, each represents a hydrogen atom, an aliphatic group or an aromatic group; and L_1, L_2, L_3, L_4, L_5, n_1, n_2 and $M^\oplus$ are as defined in the formula (I).


(IV)

wherein R_{35}, R_{36}, R_{37} and R_{38}, which may be the same or different, each represents an aliphatic group, an aromatic group or a heterocyclic group; L_{41}, L_{42} and L_{43} each represents a methine group; n_{41} represents 1, 2 or 3; and one or more of R_{35}, R_{36}, R_{37} and R_{38} have a carboxyl group or a sulfo group and the total of the carboxyl groups and/or the sulfo groups is at least two.

The dyes represented by the formula (I) are illustrated in greater detail below.

Examples of suitable aliphatic groups represented by R_1, R_2, R_3, R_4, R_5, R_6 and R_7 include a straight chain or branched alkyl group having 1 to 6 carbon atom, a cyclic alkyl group having 5 to 10 carbon atoms, aralkyl group having 7 to 10 carbon atoms, and alkenyl group having 2 to 6 carbon atoms, such as methyl, ethyl, n-butyl, benzyl, 2-sulfoethyl, 4-sulfobutyl, 2-sulfobenzyl, 2,4-disulfobenzyl, 4-sulfophenethyl, 2-carboxyethyl, carboxymethyl, trifluoromethyl, dimethylaminoethyl and 2-hydroxyethyl.

Examples of suitable aromatic groups represented by R_1, R_2, R_3, R_4, R_5, R_6 and R_7 include phenyl, naphthyl, 4-sulfophenyl, 3-sulfophenyl, 2,5-disulfophenyl, 4-carboxyphenyl and 5,7-disulfo-3-naphthyl. Of the aromatic groups, aryl groups having 6 to 10 carbon atoms are preferred.

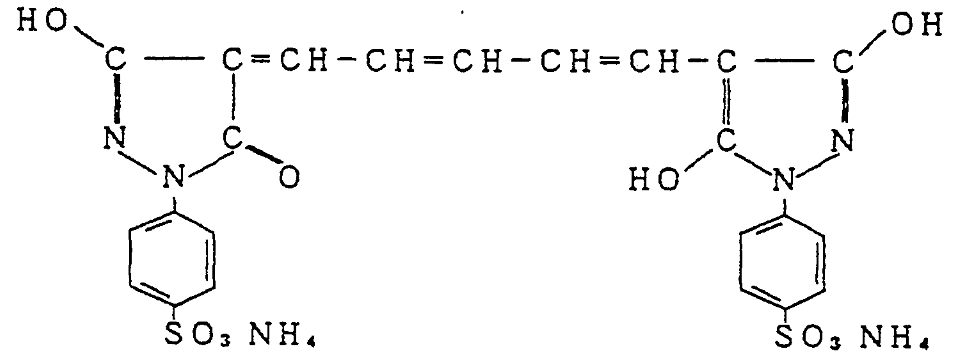
Examples of suitable 5-membered or 6-membered rings formed when R_5 and R_6 or R_6 and R_7 combine together include a pyrrolidine ring, a piperidine ring, a pyrrolidone ring and a morpholine ring.

Examples of suitable monovalent cations represented by $M^{\oplus}$ other than hydrogen include $Na^{\oplus}$, $K^{\oplus}$, $Li^{\oplus}$ and $HN(C_2H_5)_3{}^{\oplus}$.

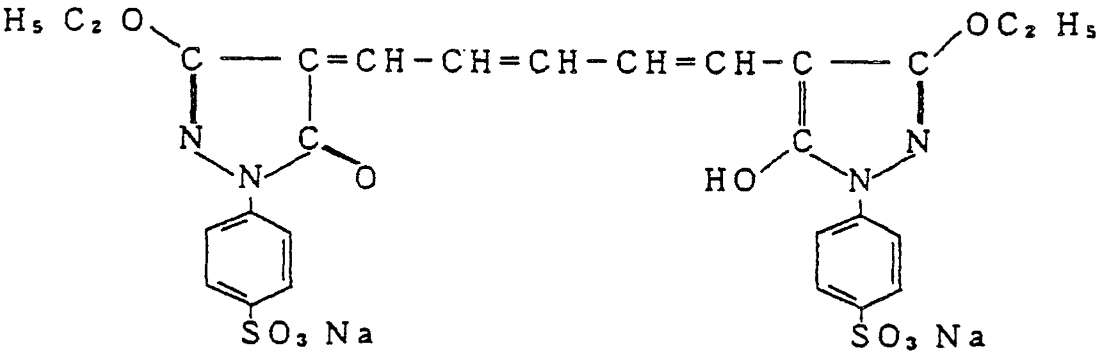
Of the compounds having the formula (I), compounds where R_1 and R_3 are an alkyl group having 1 to 6 carbon atoms and having at least 1 sulfo group or carboxyl group or an aryl group having 6 to 10 carbon atoms and having at least 1 sulfo group or carboxyl group are preferred. Particularly preferred compounds are those where R_2 and R_4 are $-OR_5$ or $-NR_5R_6$, in which R_5 and R_6 are the same as defined in the formula (I).

Examples of dyes represented by the formula (I) include the following compounds.

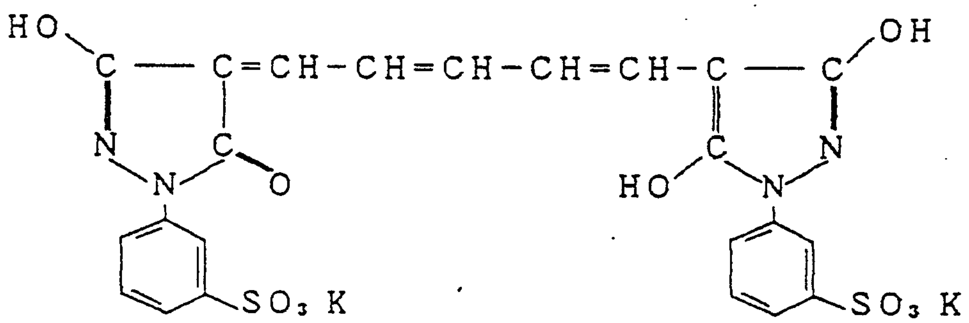
I - 1


HO
OH
C=CH-CH=CH-CH=CH-C
N
C
O
HO
N
SO3 NH4
SO3 NH4

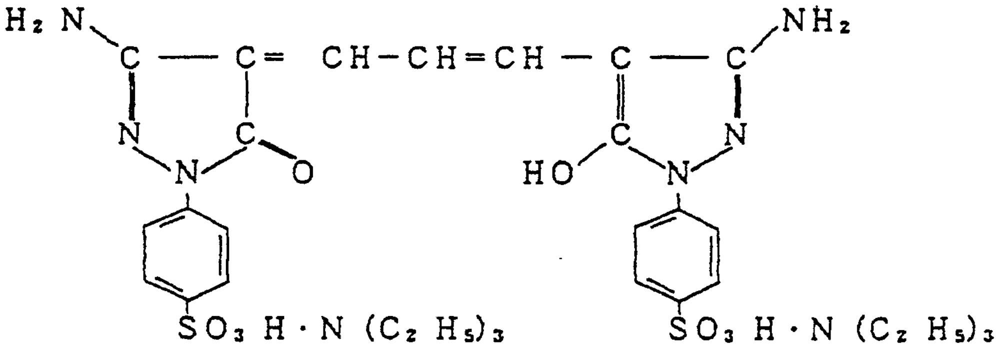
I - 2


H5 C2 O
OC2 H5
C=CH-CH=CH-CH=CH-C
N
O
HO
SO3 Na
SO3 Na

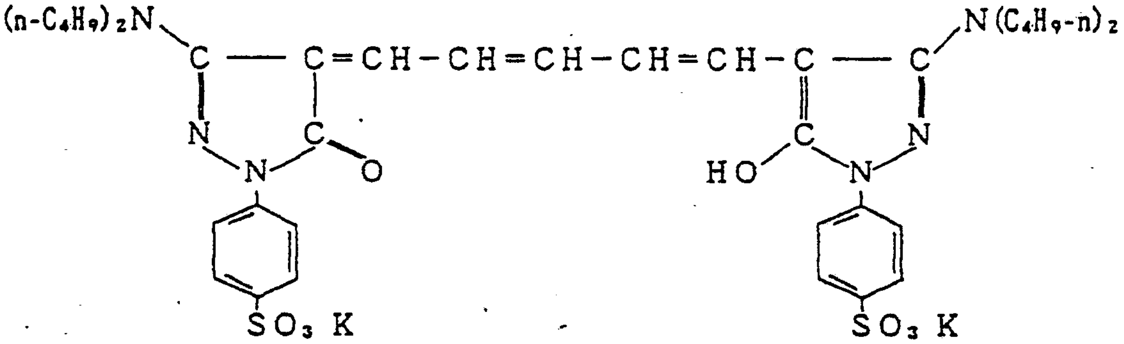
I - 3


HO
OH
C=CH-CH=CH-CH=CH-C
N
O
HO
SO3 K
SO3 K

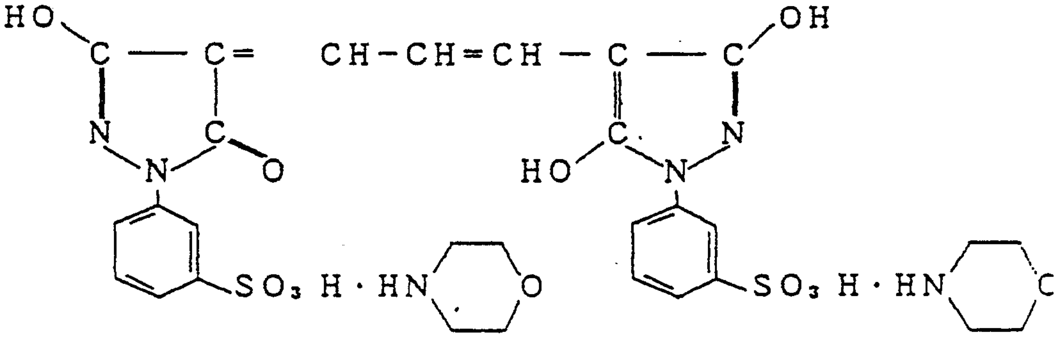
I－4


H₂N
NH₂
C═ CH－CH═CH － C
N
O
HO
SO₃H·N(C₂H₅)₃
SO₃H·N(C₂H₅)₃

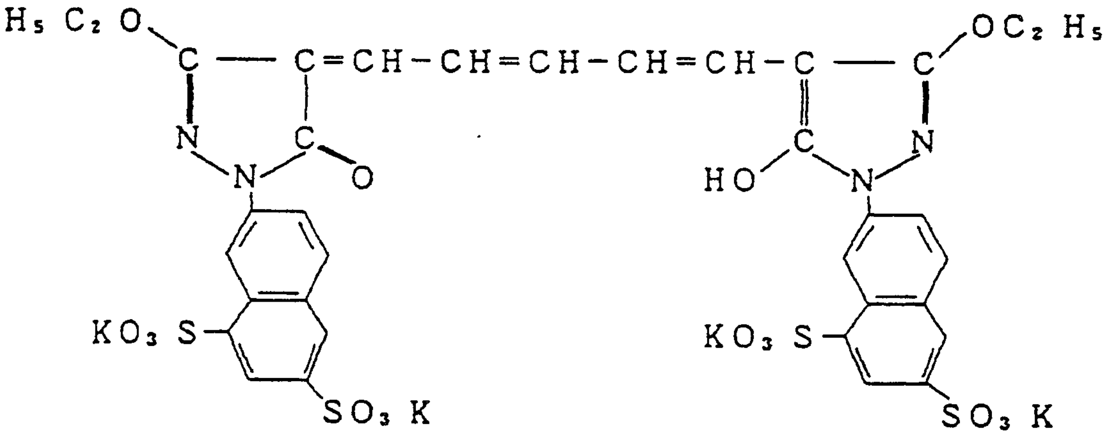
I－5


(n-C₄H₉)₂N
N(C₄H₉-n)₂
C═CH－CH═CH－CH═CH－C
N
O
HO
SO₃K
SO₃K

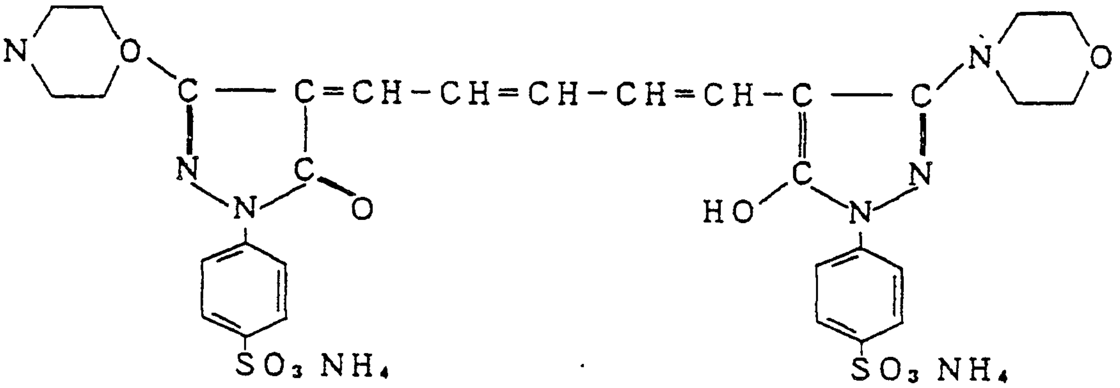
I－6


HO
OH
C═ CH－CH═CH － C
N
O
HO
SO₃H·HN
SO₃H·HN

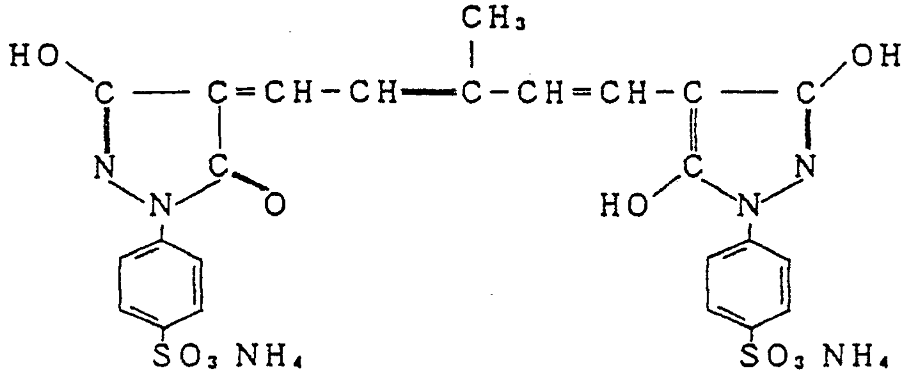
I－7



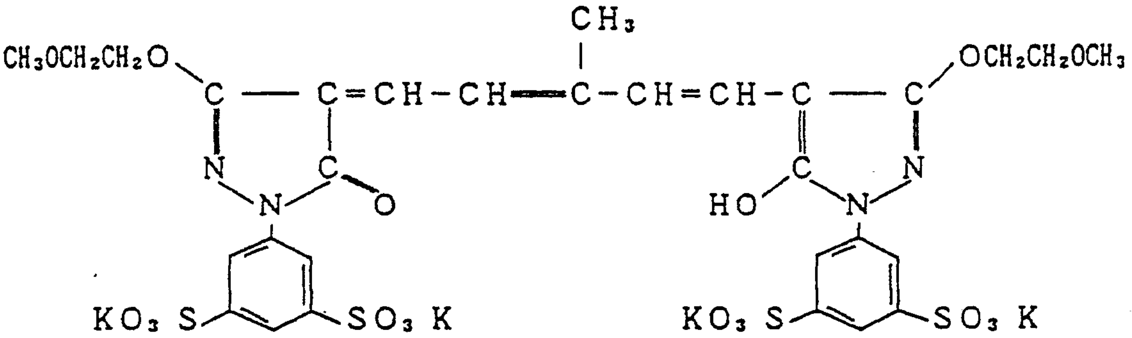
I－8



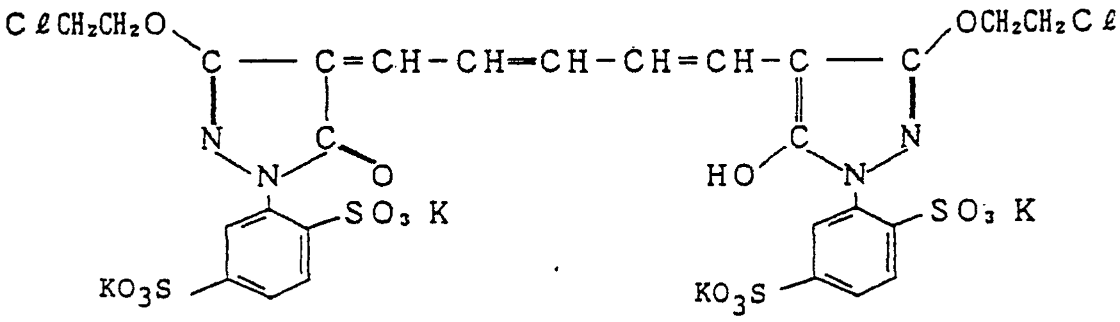
I－9



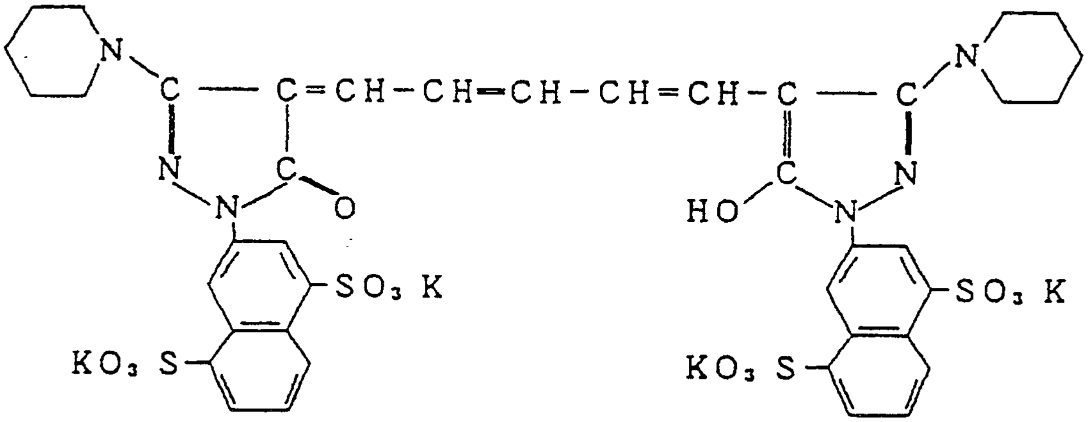
I－10



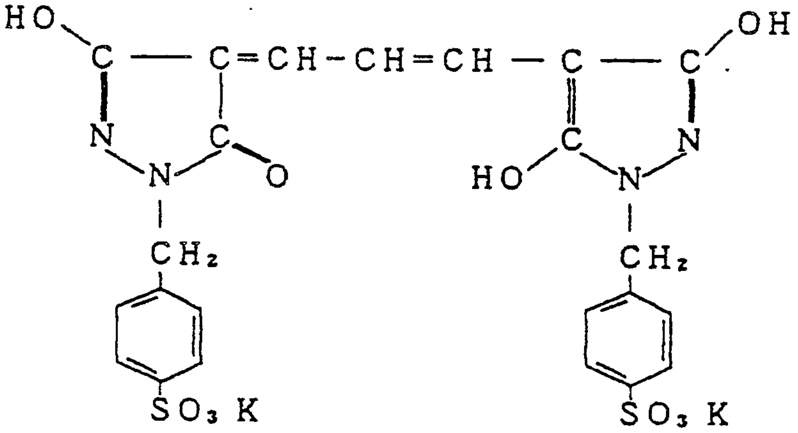
I－11



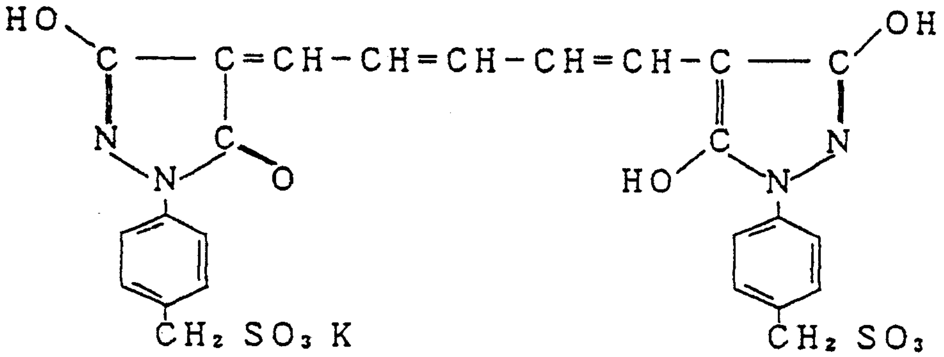
I－12


N
C
C=CH−CH=CH−CH=CH−C
C
N
N
C
O
SO₃ K
KO₃ S
N
C
N
C
HO
N
SO₃ K
KO₃ S

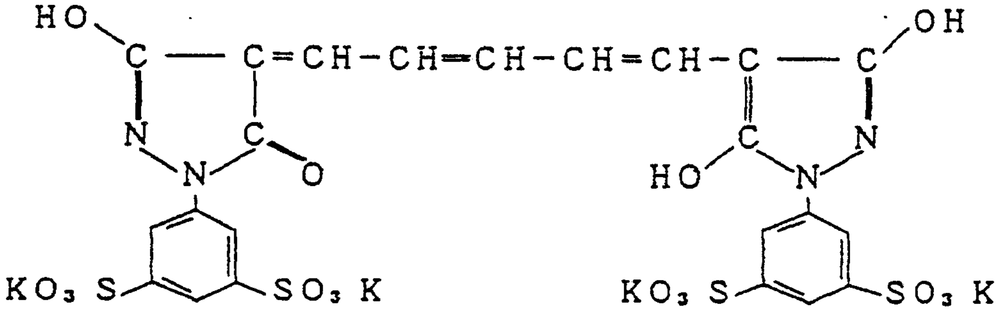
I－13


HO
C
C=CH−CH=CH
C
C
OH
N
C
N
O
CH₂
SO₃ K
HO
C
N
N
CH₂
SO₃ K

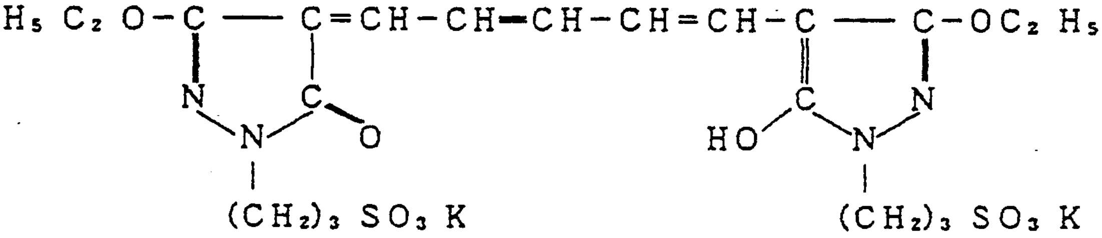
I－14



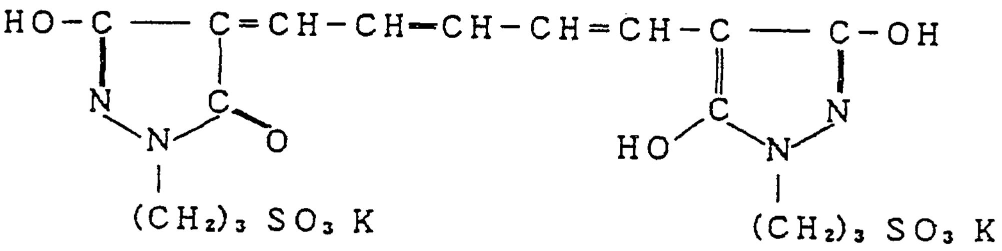
I－15



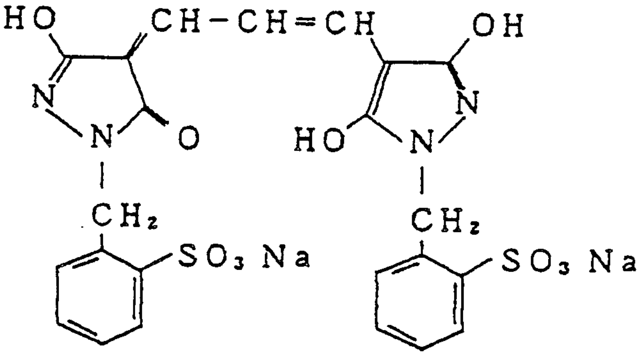
I－16



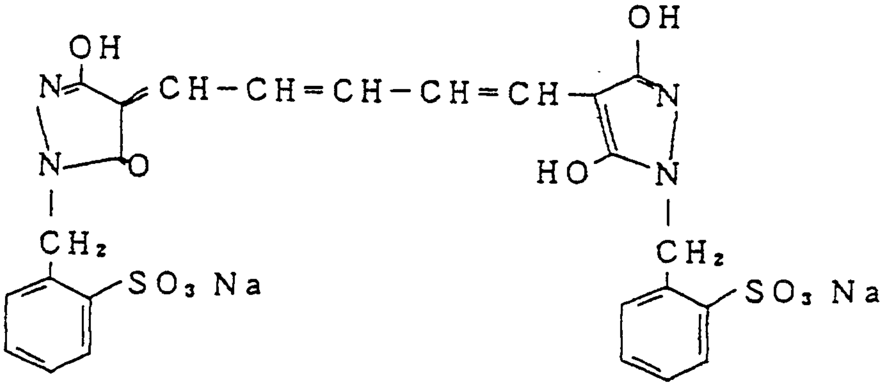
I－17



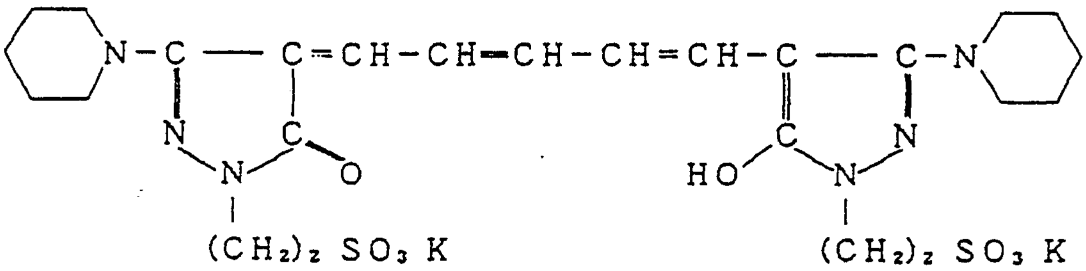
I－18



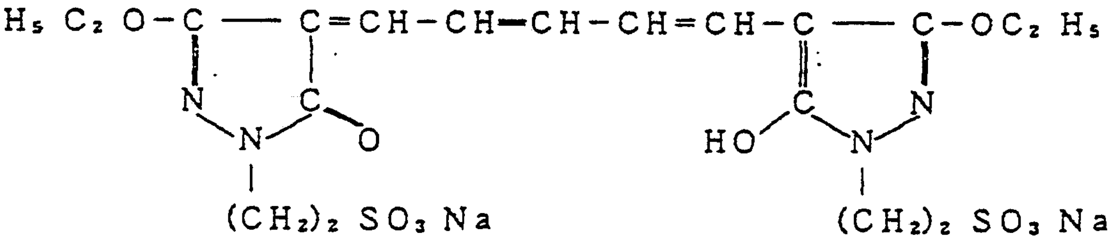
I－19

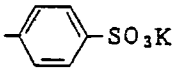
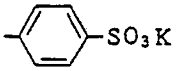
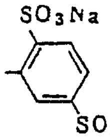
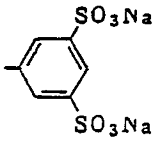
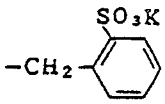
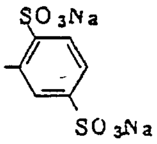
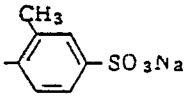
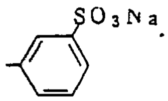


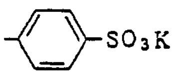
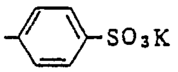
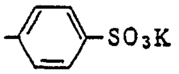
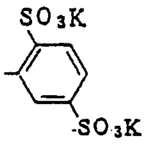
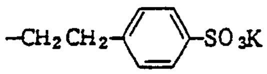
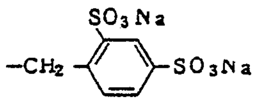
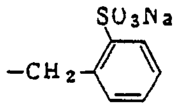
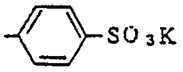
I－20

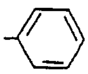
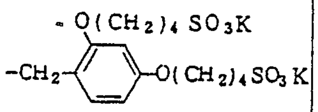
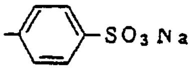
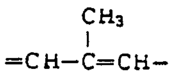
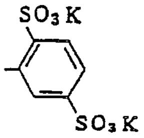
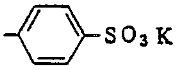
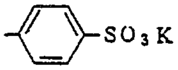
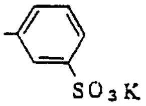
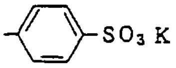
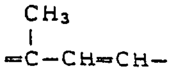
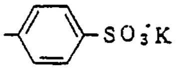


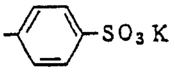
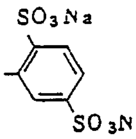
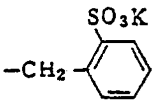
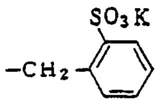
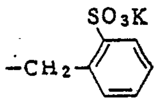
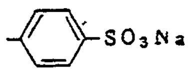
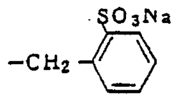
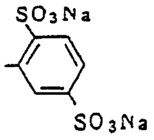
I－21



№	R_1、R_3	R_2、R_4	$=(L_1-L_2)_{n_1}=L_3+L_4=L_5)_{n_2}-$	$M^{\ominus}$
I-22		$-CH_3$	$=CH-$	H
-23		$-CONHC_3H_7^{(n)}$	$=CH-$	H
-24		$-OH$	$=CH-CH=CH-$	Na
- 25		$-OC_2H_5$	$=CH+CH=CH+_2$	Na
-26	$-CH_2CH_2SO_3K$	$-COOC_2H_5$	$=CH-CH=CH-$	H
-27		$-CONHC_4H_9^{(n)}$	$=CH-CH=CH-$	H
-28	$-CH_2CH_2SO_3K$	$-COOK$	$=CH+CH=CH+_2$	H
-29		$-COCH_3$	$=CH+CH=CH+_2$	Na
- 30		$-CF_3$	$=CH+CH=CH+_2$	H
- 31		$-NHCOCH_3$	$=CH-CH=CH-$	H

№	R_1, R_3	R_2, R_4	$=(L_1-L_2)_{n_1}=L_3(L_4=L_5)_{n_2}-$	$M^{\ominus}$
I-32		$-COOC_2H_5$	$=CH(CH=CH)_2$	H
-33		$-COOK$	$=CH-CH=CH-$	H
-34		$-NHCONHCH_3$	$=CH-CH=CH-$	H
-35	$-(CH_2)_4SO_3K$	$-OH$	$=CH-$	H
-36		$-COOK$	$=CH-CH=CH-$	K
-37		$-C_6H_5$	$=CH-CH=CH-$	H
-38		$-COOC_2H_5$	$=CH(CH=CH)_2$	Na
-39		$-CONHCH_2CH_2OH$	$=CH(CH=CH)_2$	H
-40		$-CONHCH_2CH_2SO_3K$	$=CH(CH=CH)_2$	H
-41	$-(CH_2)_3SO_3K$	$-CONHC_7H_{15}{}^{(n)}$	$=CH-CH=CH-$	H
-42	$-CH_2COOK$	$-COOK$	$=CH-CH=CH-$	K
-43	$-CH_2CH_2SO_3K$	$-N(CH_3)_2$	$=CH(CH=CH)$	H

No.	R_1, R_3	R_2, R_4	$-(L_1-L_2)_{n_1}=L_3(L_4=L_5)_{n_2}-$	$M^{\oplus}$
I-44	$-(CH_2)_3SO_3K$		$=CH(CH=CH)_2$	H
-45		$-CH_2Cl$	$=CH(CH=CH)_2$	H
-46	$-(CH_2)_2SO_3Na$	$-OH$	$=CH(CH=CH)_2$	H
-47		$-CH_3$	 $=CH-\overset{\overset{CH_3}{\vert}}{C}=CH-$	Na
-48		$-SO_2CH_3$	$=CH(CH=CH)_2$	K
-49		$-CONHC_2H_5$	$=CH-CH=CH-$	H
-50		$-NHCOC_3H_7^{(i)}$	$=CH-CH=CH-$	H
-51	$-CH_2CH_2SO_3K$		$=CH-CH=CH-$	H
-52		$-CH_3$	 $=\overset{\overset{CH_3}{\vert}}{C}-CH=CH-$	H
-53		$-{}^tC_4H_9$	$=CH-CH=CH-$	H

№	R_1, R_3	R_2, R_4	$-(L_1-L_2)_{n_1}-L_3(L_4-L_5)_{n_2}-$	$M^{\oplus}$
I-54		$-CN$	$=CH-CH=CH-CH=CH-$	H
-55		$-COCH_3$	$=CH-CH=\overset{CH_3}{\overset{\vert}{C}}-CH=CH-$	Na
-56		$-COOK$	$=CH(CH=CH)_2$	H
-57		$-COOK$	$=CH-CH=CH-$	H
-58		$-CONHC_4H_9^{(i)}$	$=CH(CH=CH)_2$	H
-59		$-NHSO_2CH_3$	$=CH(CH=CH)_2$	H
-60		$-CONHCH_2CH_2OH$	$=CH-CH=CH-$	H
-61		$-COOC_2H_5$	$=CH(CH=CH)_2$	H

These dyes can be synthesized according to the methods described in British Patents 506,385, 1,777,429, 1,338,799, 1,385,371, 1,467,214, 1,433,102 and 1,553,516, JP-A-48-85130, JP-A-55-161233, JP-A-52-20330, JP-A-59-111640, JP-A-62-273527 and JP-A-63-139949.

The syntheses of these compounds are illustrated by the following synthesis examples. Unless otherwise indicated herein, all parts, percents, ratios and the like are by weight.

SYNTHESIS EXAMPLE I-1

Dye I-1:

A mixture of 5.1 g of 3-hydroxy-1-(4′-sulfophenyl)-5-pyrazolone, 2.8 g of N-(2,4-dinitrophenyl)pyridinium hydrochloride and 50 ml of ethanol was saturated with ammonia gas at a temperature of 10 to 20° C with stirring to obtain a uniform solution. The solution was stirred for 24 hours to precipitate dark greenish blue crystals. The crystals were collected by filtration, thoroughly washed with ethanol and then acetone and dried to obtain 5.8 g of the desired dye. An aqueous solution of the dye had a maximum absorption wavelength of 584 nm.

SYNTHESIS EXAMPLE I-2

Dye I-2:

153 g of sodium salt of 3-ethoxy-1-(4′-sulfophenyl)-5-pyrazolone was dissolved in 1.5 liters of methanol and 100 g of triethylamine. 71 g of glutacondialdehydodianil hydrochloride was added thereto and the mixture was stirred at room temperature for 5 hours. After standing overnight, 3 liters of ethyl acetate was added thereto. The precipitated crystals were recovered by filtration, thoroughly washed with ethanol and then acetone and dried to obtain 47 g of the desired dye. An aqueous solution of the dye had a maximum absorption wavelength of 598 nm.

SYNTHESIS EXAMPLE I-3

Dye I-4:

36 g of 3-amino-1-(4′-sulfophenyl)-5-pyrazolone was dissolved in 250 ml of methanol and 30 g of triethylamine. While cooling the resulting solution with ice, 14 g of malonaldehydodianil hydrochloride was added thereto and the mixture was vigorously stirred. The stirring was continued for 3 hours. The precipitated crystals were recovered by filtration, washed with methanol and dried to obtain 46 g of the desired dye. An aqueous solution of the dye had a maximum absorption wavelength of 505 nm.

SYNTHESIS EXAMPLE I-4

Dye I-9:

A mixture of 5.1 g of 3-hydroxy-1-(4′-sulfophenyl)-5-pyrazolone, 2.9 g of N-(2,4-dinitrophenyl)-γ-picolinium hydrochloride and 50 ml of ethanol was saturated with ammonia gas at a temperature of 10 to 20 °C with stirring to obtain a uniform solution. After the solution was stirred for 24 hours, the precipitated crystals were recovered by filtration, thoroughly washed with ethanol and then acetone and dried to obtain 5.0 g of the desired dye. An aqueous solution of the dye had a maximum absorption wavelength of 607 nm.

SYNTHESIS EXAMPLE I-5

Synthesis of Dye I-16:

A mixture of 5 g of 3-ethoxy-1-(3′-sulfopropyl)-5-pyrazolone, 2.8 g of glutacondialdehydodianil hydrochloride, 100 ml of methanol and 4 g of triethylamine was stirred at a temperature of 30 to 40 °C for 3 hours. 20 ml of a methanol solution of 2 g of anhydrous potassium acetate was added thereto with stirring to form a blue precipitate. After stirring for 1 hour, the precipitate was collected by filtration, thoroughly washed with acetone and dried to obtain 4.3 g of the desired dye. An aqueous solution of the dye was blue and had a maximum absorption wavelength of 596 mμ.

The dyes represented by the formula (II) are illustrated in greater detail below.

Examples of suitable aliphatic groups represented by R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18} or R_{19} are alkyl groups having 1 to 6 carbon atoms and aralkyl groups having 7 to 10 carbon atoms and include methyl, ethyl, isopropyl, 2-chloroethyl, trifluoromethyl, benzyl, 2-sulfobenzyl, 4-sulfophenethyl, carboxymethyl, 2-carboxyethyl, 2-sulfoethyl, 2-hydroxyethyl, dimethylaminoethyl and cyclopentyl.

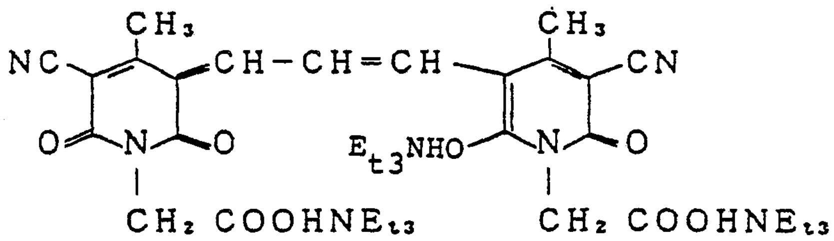
Examples of suitable aromatic groups represented by R_{11}, R_{13}, R_{14}, R_{16}, R_{17}, R_{18} or R_{19} are aryl groups having 6 to 10 carbon atoms and include phenyl, naphthyl, 3-sulfophenyl, 4-sulfophenyl, 2,5-disulfophenyl, 4-(3-sulfopropyloxy)phenyl, 3-carboxyphenyl and 2-carboxyphenyl.

Examples of suitable heterocyclic groups represented by R_{11}, R_{13}, R_{14} or R_{16} include 2-pyridyl, morpholino and 5-sulfobenzimidazole-2-yl.

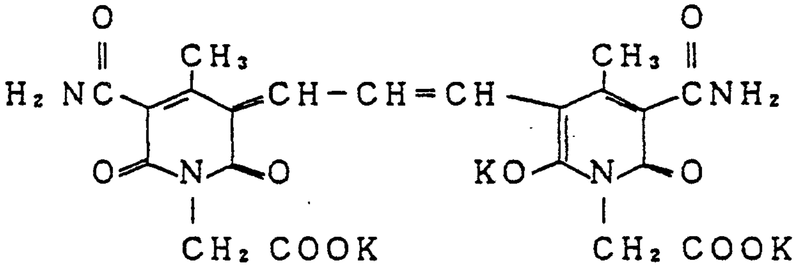
Examples of suitable 5-membered or 6-membered rings formed when R_{17} and R_{18} or R_{18} and R_{19} combine together include piperidine, pyrrolidine, morpholine and pyrrolidone.

Examples of dyes represented by the formula (II) include the following compounds.

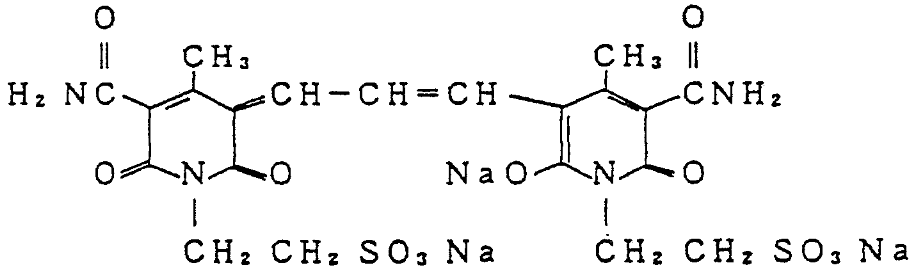
(II - 1)



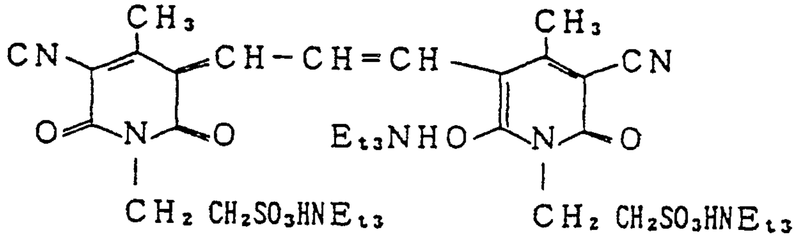
(II - 2)



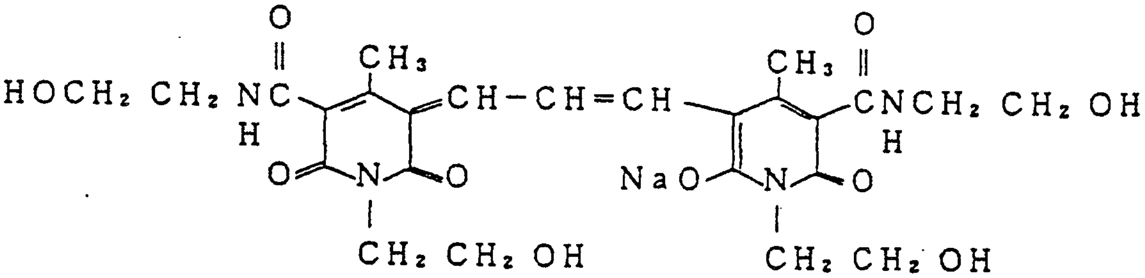
(II - 3)



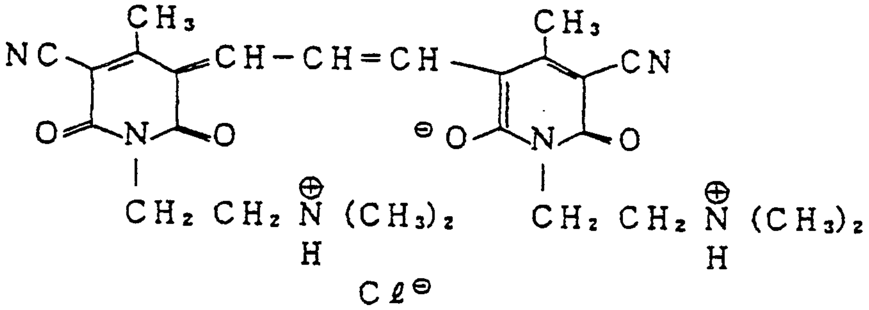
(II－4)



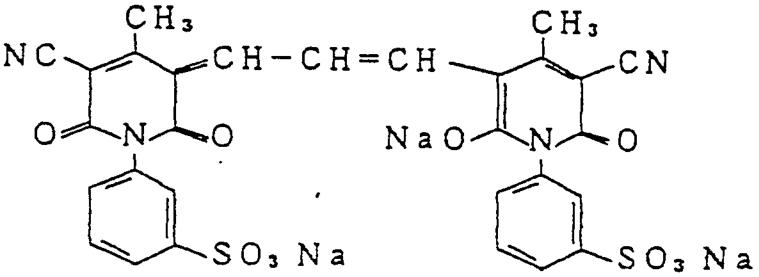
(II－5)



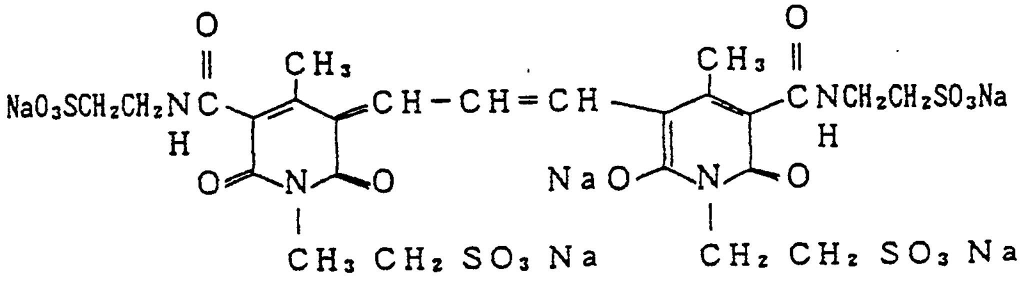
(II－6)



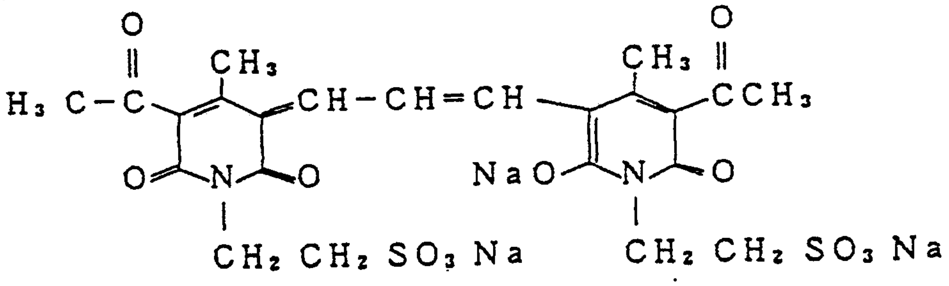
(II－7)



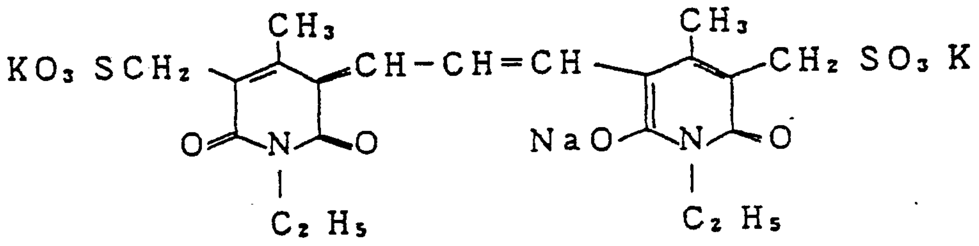
(II－8)



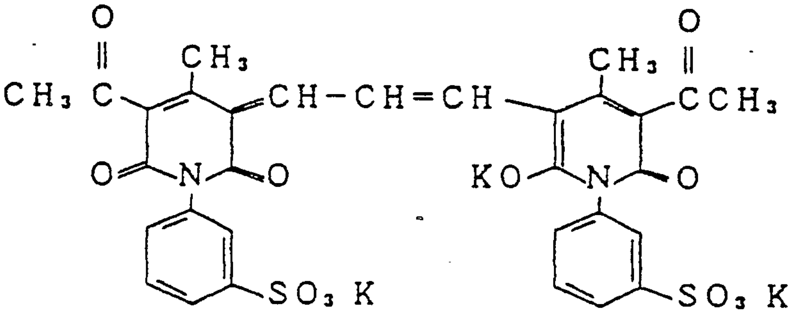
(II－9)



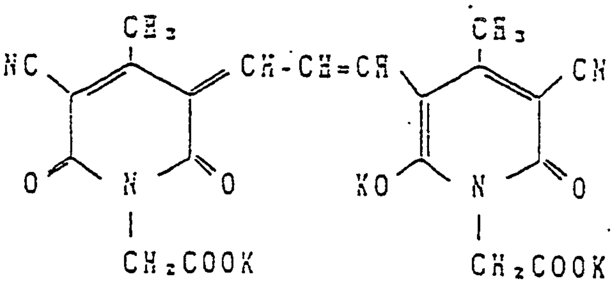
(II－10)



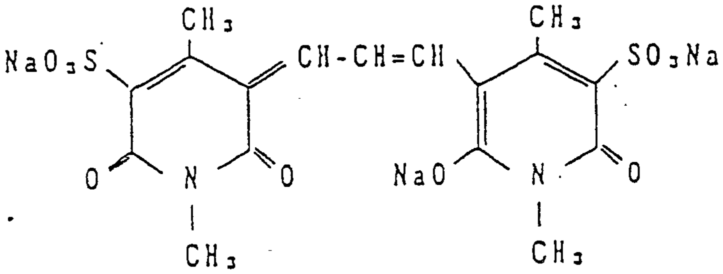
(II-11)



(II-12)



(II-13)



Dyes having the formula (II) can be synthesized according to the methods described in British Patents 1,278,621, 1,512,863 and 1,579,899 and in accordance with the following synthesis examples.

SYNTHESIS EXAMPLE II-1

Synthesis of Dye (II-10):

1.6 ml of acetic anhydride was added dropwise to a mixture of 4.0 g of monosodium salt of 1-ethyl-6-hydroxy-4-methyl-3-sulfomethylpyrido-2-one, 1.9 g of malonaldehydodianil hydrochloride, 5.0 ml of triethylamine and 120 ml of isopropyl alcohol. The mixture was stirred at room temperature overnight. The formed precipitate was collected by filtration and dissolved in a mixed solvent of water/methanol = 1/3 (by volume). A solution of 1.4 g of potassium acetate in ethanol was added dropwise to the resulting solution. The formed precipitate was recovered by filtration and dried under reduced pressure. Yield: 1.1 g. Maximum Absorption in water: 592 nm. Melting Point: ≥300° C.

SYNTHESIS EXAMPLE II-2

Synthesis of Dye (II-1):

An ethanol solution of 3.0 g of 1-carboxymethyl-3-cyano-6-hydroxy-4-methylpyrido-2-one, 1.3 g of 1,3,3-trimethoxypropene and 2.8 ml of triethylamine was heated at reflux for 2 days. The mixture was then cooled to room temperature and the resulting precipitate was recovered by filtration and dried to obtain 1.5 g of the desired Dye (II-1). Maximum Absorption in water: 610 nm.

SYNTHESIS EXAMPLE II-3

Synthesis of Dye (II-7):

5.6 g of 3-cyano-6-hydroxy-4-methyl-1-(2-sulfoethyl)-pyrido-2-one, 4.5 g of malonaldehydodianil hydrochloride and 6.9 ml of triethylamine were dissolved in 50 ml of methanol. The temperature of the resulting solution was brought to 5° C or below. 3.1 ml of acetic anhydride was added dropwise to the solution and the mixture was stirred for 13 hours. The resulting precipitate was recovered by filtration, washed with 50 ml of acetonitrile and 1.0 ml of triethylamine with heating and dried to obtain 1.9 g of Dye (II-7). Maximum Absorption in N,N-dimethylformamide: 625 nm.

The dyes represented by the formula (III) are illustrated in greater detail below.

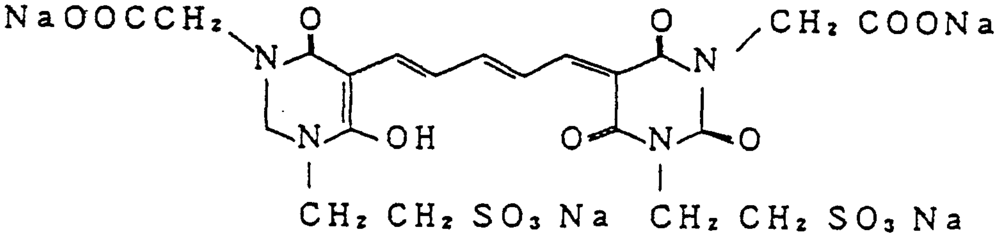
Suitable aliphatic groups represented by R_{31}, R_{32}, R_{33} and R_{34} are the same as those described for R_1, R_2, R_3 and R_4 in the formula (I).

Suitable aromatic groups represented by R_{31}, R_{32}, R_{33} and R_{34} are the same as those described for R_1, R_2, R_3 and R_4 in the formula (I).

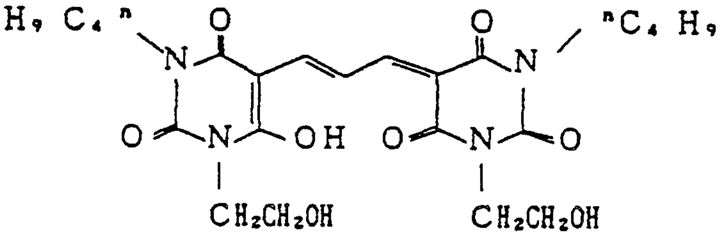
Suitable heterocyclic groups represented by R_{31}, R_{32}, R_{33} and R_{34} are the same as those described for R_1, R_2, R_3 and R_4 in the formula (I).

Examples of the dyes having the formula (III) include the following compounds.

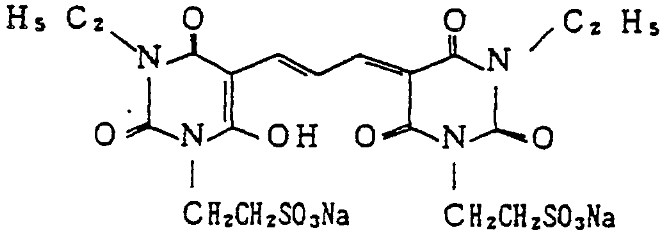
Ⅲ－1


NaOOCCH₂
O
N
N
OH
CH₂ CH₂ SO₃ Na
O
N
CH₂ COONa
O
N
O
CH₂ CH₂ SO₃ Na

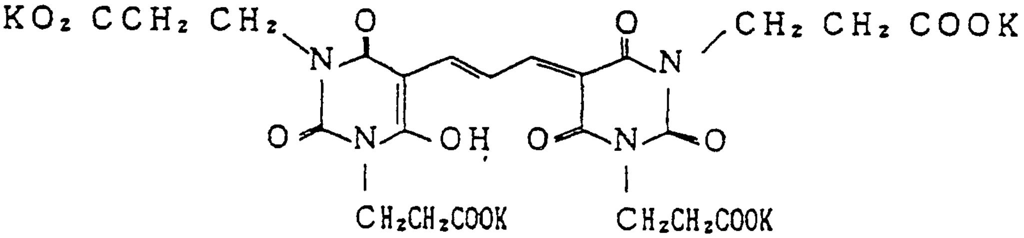
Ⅲ－2


H₉ C₄ ⁿ
O
N
O
N
OH
CH₂CH₂OH
O
N
ⁿC₄ H₉
O
N
O
CH₂CH₂OH

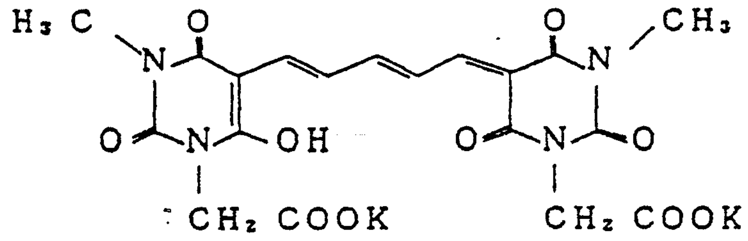
Ⅲ－3


H₅ C₂
O
N
O
N
OH
CH₂CH₂SO₃Na
O
N
C₂ H₅
O
N
O
CH₂CH₂SO₃Na

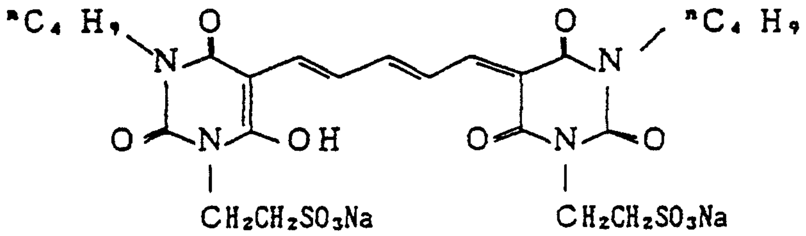
Ⅲ－4


KO₂ CCH₂ CH₂
O
N
O
N
OH
CH₂CH₂COOK
O
N
CH₂ CH₂ COOK
O
N
O
CH₂CH₂COOK

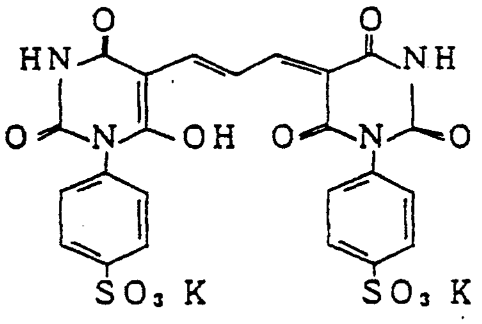
Ⅲ－5



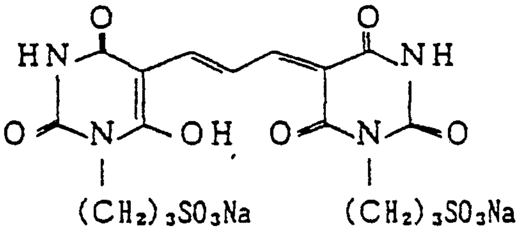
Ⅲ－6



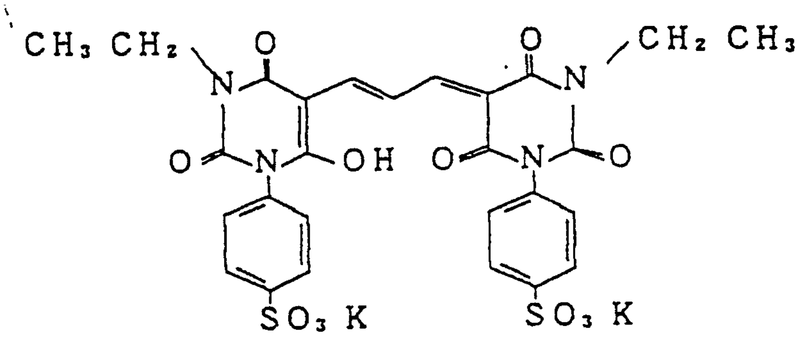
Ⅲ－7



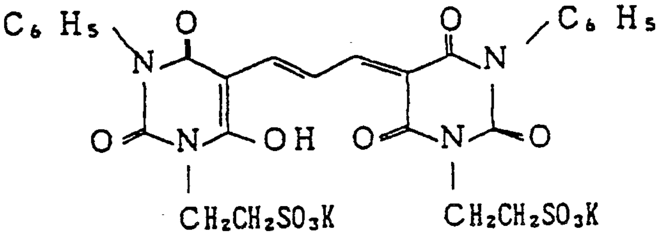
Ⅲ－8



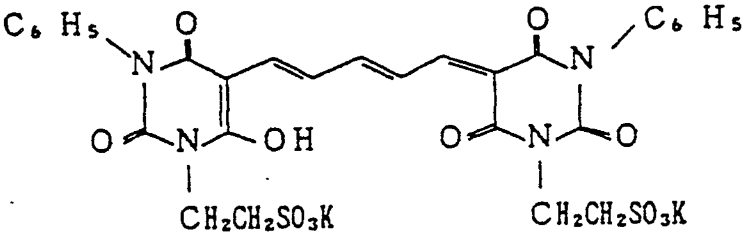
Ⅲ－9



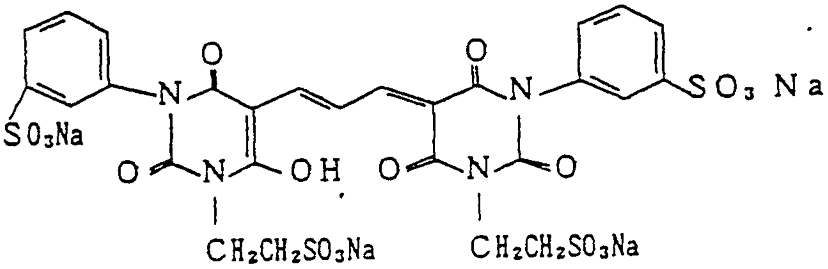
Ⅲ－10



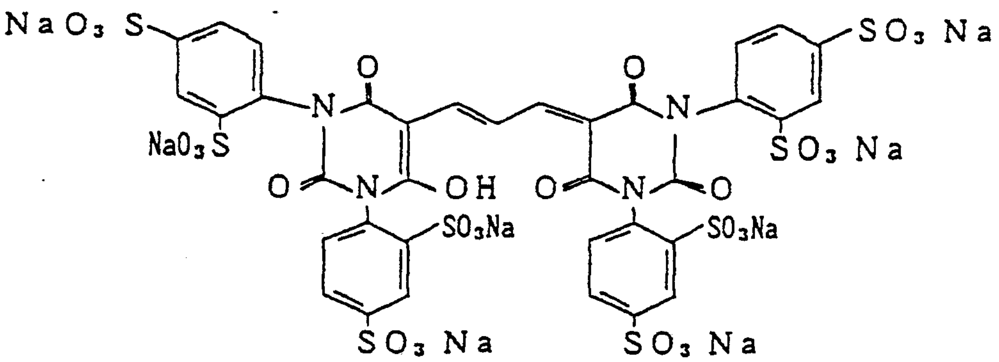
Ⅲ－11



Ⅲ－12



Ⅲ-13



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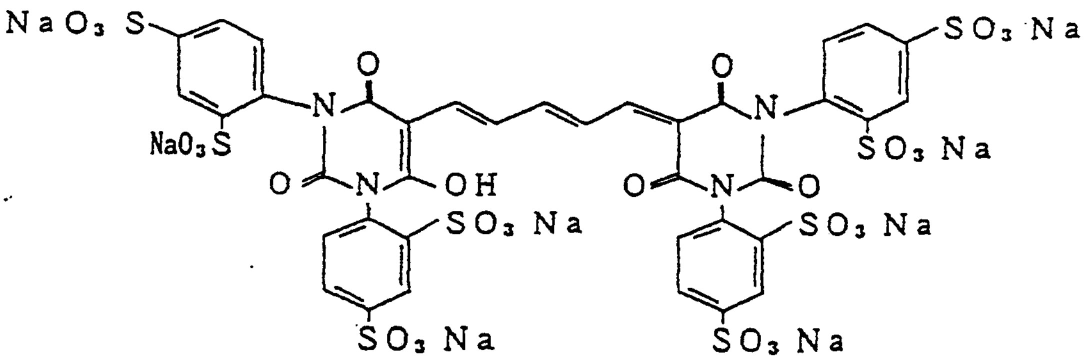


These dyes of the formula (III) can be synthesized according to the methods described in U.S. Patents 3,247,127, 3,469,985, 3,653,905 and 4,078,933.

Synthesis of these compounds is illustrated by the following synthesis examples.

SYNTHESIS EXAMPLE III-1

Dye III-3:

A suspension of 5.7 g of N-ethyl-N′-(2-sulfoethyl)barbituric acid, 1.7 g of tetramethoxypropane and 10 ml of pyridine was stirred at reflux to dissolve them. 2.5 ml of triethylamine was added dropwise thereto and the mixture was stirred. The reaction mixture was cooled to room temperature and 500 ml of acetone was added thereto. The mixture was thoroughly stirred. The precipitated oily product was separated by decantation and dissolved in 15 ml of methanol. 10 ml of a solution of 2.5 g of sodium iodide in methanol was added thereto. The mixture was heated for 5 minutes and cooled with water. The precipitated crystals were collected by filtration, thoroughly washed with acetone and dried to obtain 4.3 g of reddish brown crystals. An aqueous solution of the dye was red and had a maximum absorption wavelength of 490 nm.

SYNTHESIS EXAMPLE III-2

Dye III-6:

A mixture of 5.7 g of N-(n-butyl)-N′-(2-sulfoethyl)barbituric acid, 2.4 g of glutaconic aldehyde dianil hydrochloride, 50 ml of pyridine and 10 ml of triethylamine was heated with stirring on a water bath for 30 minutes. The reaction mixture was filtered during heating. A solution of 2.6 g of sodium iodide in methanol was added to the filtrate. The mixture was cooled with water. The precipitated crystals were recovered by filtration, thoroughly washed with acetone and dried to give 4.1 g of blue crystals. An aqueous solution of the dye was bluish purple and maximum absorption wavelength was 589 nm.

SYNTHESIS EXAMPLE III-3

Dye III-10:

A mixture of 6.2 g of N-phenyl-N′-(2-sulfoethyl)barbituric acid, 2.5 g of malonaldehydodianil hydrochloride, 10 ml of triethylamine and 50 ml of methanol was stirred under reflux for 30 minutes. 20 ml of a solution of 2.0 g of anhydrous potassium acetate in methanol was added thereto. The mixture was stirred for 5 minutes and cooled with water. The precipitated crystals were collected by filtration, thoroughly washed with acetone and dried to give 4.8 g of reddish brown crystals. An aqueous solution of the dye was reddish brown and maximum absorption wavelength was 490 nm.

SYNTHESIS EXAMPLE III-4

Dye III-11:

A mixture of 6.2 g of N-phenyl-N′-(2-sulfoethyl)barbituric acid, 2.8 g of glutaconic aldehyde dianil hydro chloride, 15 ml of triethylamine and 50 ml of methanol was stirred at reflux for 20 minutes. 20 ml of a solution of 2.0 g of anhydrous potassium acetate was added thereto. The mixture was stirred for 5 minutes and cooled with water. The precipitated crystals were collected by filtration, thoroughly washed with acetone and dried to give 5.3 g of blue crystals.

An aqueous solution of the dye was bluish purple and maximum absorption wavelength was 590 nm.

SYNTHESIS EXAMPLE III-5

Dye III-14:

A mixture of 7.2 g of sodium salt of N,N′-bis(2,3-disulfophenyl)barbituric acid, 2.8 g of glutaconic aldehyde dianil hydrochloride, 15 ml of triethylamine and 80 ml of methanol was stirred at reflux for 30 minutes. The reaction mixture was concentrated at room temperature under reduced pressure until the volume thereof was reduced to 1/3. 200 ml of isopropanol was added thereto. The precipitated crystals were collected by filtration, thoroughly washed with acetone and dried to give 6.1 g of blue crystals.

An aqueous solution of the dye was bluish purple and maximum absorption wavelength was 590 nm.

The dyes represented by the formula (IV) are illustrated in greater detail below.

R_{35}, R_{36}, R_{37} and R_{38} in the dyes having the formula (IV) each represents an alkyl group having 1 to 6 carbon atoms (e.g., methyl, ethyl, carboxymethyl, 2-carboxyethyl, 2-hydroxyethyl, methoxyethyl, 2-chloroethyl, benzyl, 2-sulfobenzyl, 4-sulfophenethyl), an aryl group having 6 to 10 carbon atoms (e.g., phenyl, 4-sulfophenyl, 3-sulfophenyl, 2-sulfophenyl, 4-carboxyphenyl, 3-carboxyphenyl, 4-hydroxyphenyl) or a residue of a heterocyclic ring (e.g., 2-pyridyl, 2-imidazolyl).

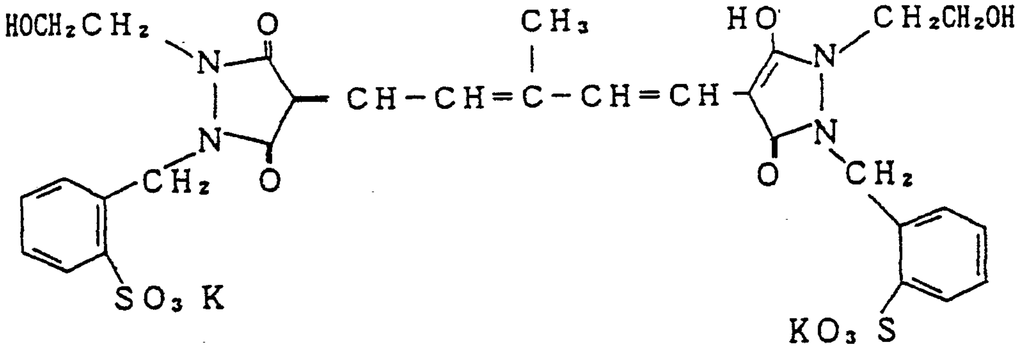
L_{41}, L_{42} and L_{43} each represents a methine group. These methine groups may be independently substituted by methyl, ethyl, phenyl, sulfoethyl, carboxyethyl or the like.

n_{41} represents 1, 2 or 3.

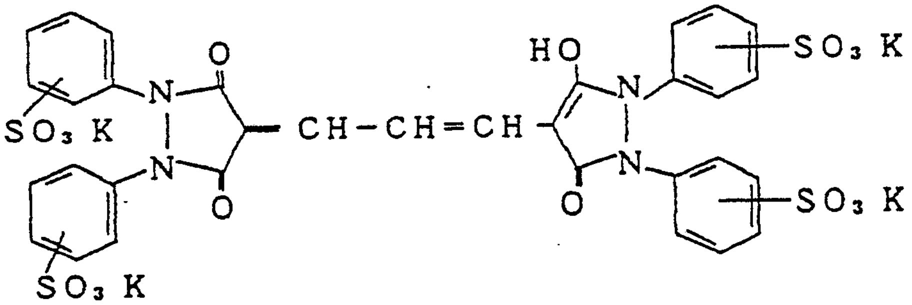
One or more of R_{35}, R_{36}, R_{37} and R_{38} have at least one carboxyl or sulfo group and the total of the carboxyl groups and/or sulfo groups is at least 2. The carboxyl group and the sulfo group may be in the free form or in the form of a salt (e.g., Na salt, K salt, ammonium salt).

Examples of dyes having the formula (IV) which can be used in the present invention include the following compounds.

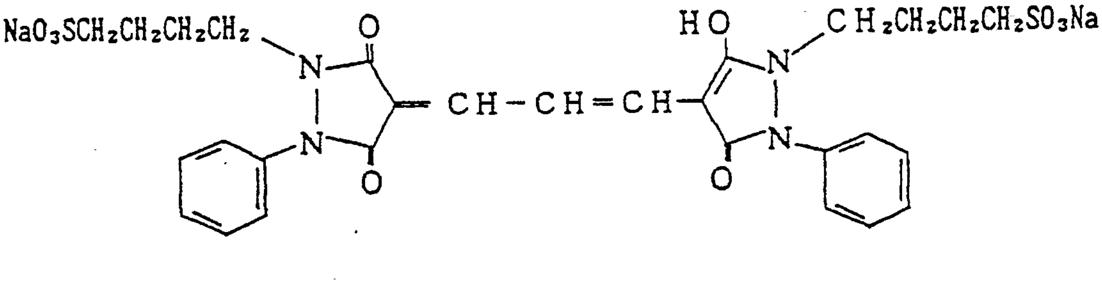
(IV-1)



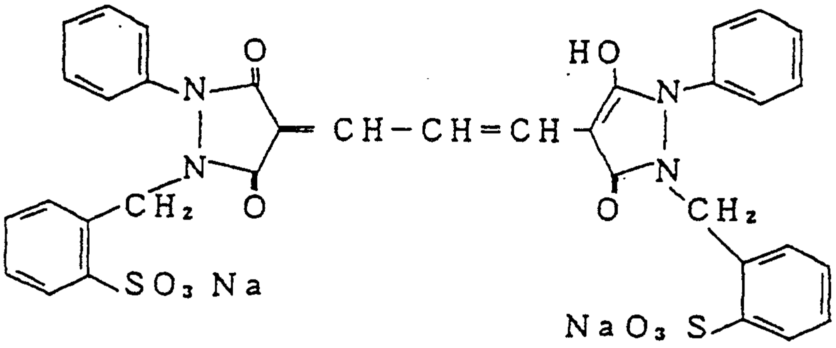
(IV-2)



(IV-3)

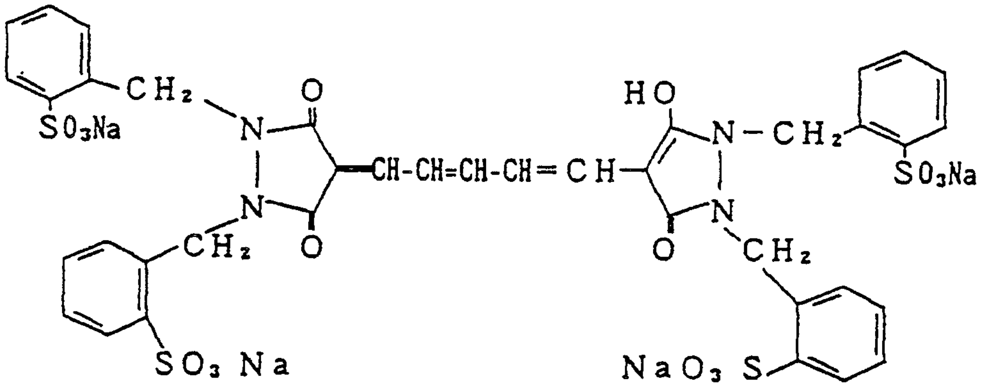


(IV－4)



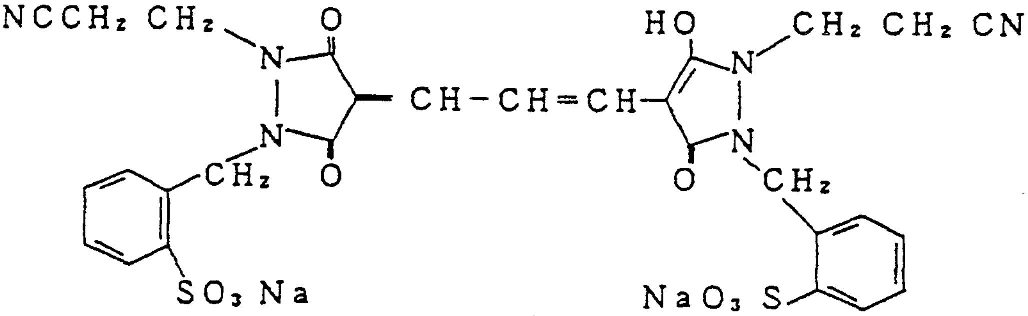
O
N
N
CH₂
O
SO₃Na
CH－CH＝CH
HO
N
N
O
CH₂
NaO₃S

(IV－5)



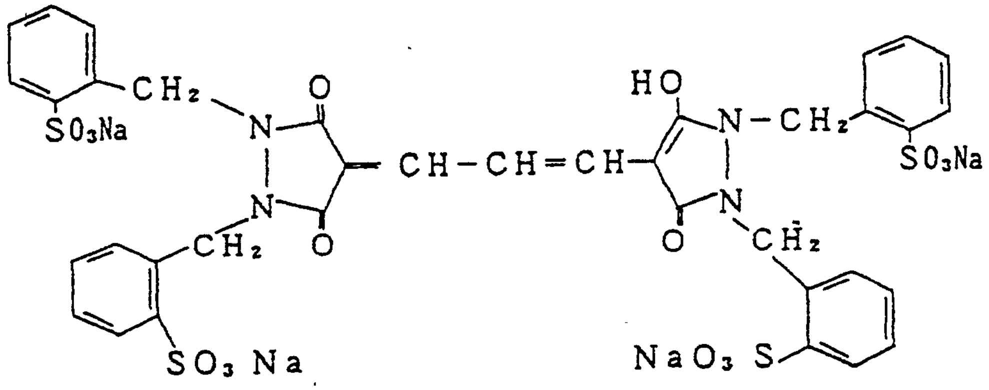
CH₂
SO₃Na
N
O
N
CH₂
O
SO₃Na
CH-CH=CH-CH＝CH
HO
N－CH₂
SO₃Na
N
O
CH₂
NaO₃S

(IV－6)

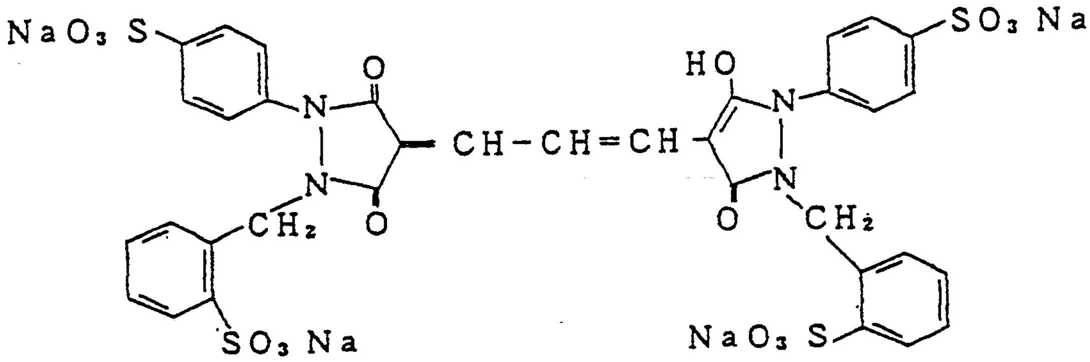


NCCH₂CH₂
N
O
N
CH₂
O
SO₃Na
CH－CH＝CH
HO
CH₂CH₂CN
N
N
O
CH₂
NaO₃S

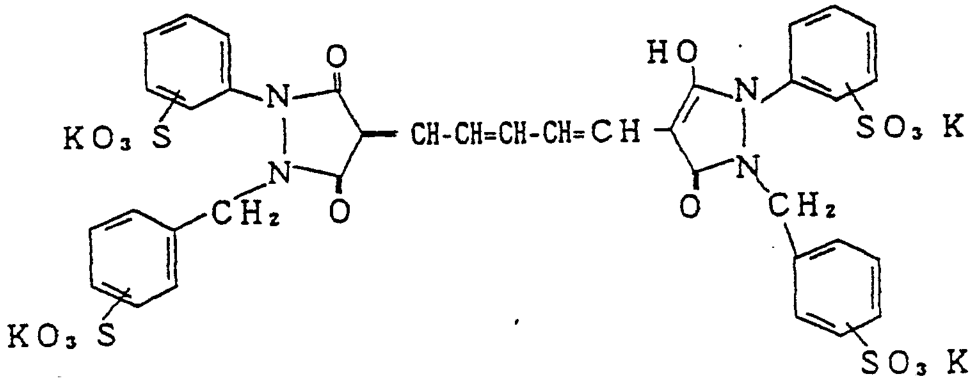
(IV-7)



(IV-8)



(IV-9)



The following synthesis examples illustrate the production of the compounds of the formula (IV) of the present invention without limiting the invention thereto.

SYNTHESIS EXAMPLE IV-1

Compound (IV-2) of the Invention:

16.7 g of 1,2-diphenyl-3,5-pyrazolidinedione was added to 48 ml of concentrated sulfuric acid and 36 ml of 20% fuming sulfuric acid. The mixture was heated on a steam bath for 4 hours. After cooling, the mixture was poured into ice and neutralized with a potassium hydroxide solution. The precipitated crystals were collected by filtration and washed with methanol to give 27 g of a sulfonated product of 1,2-diphenyl-3,5-pyrazolidinedione.

9.7 g of the sulfonated product of 1,2-diphenyl-3,5-pyrazolidinedione, 1.3 g of tetramethoxypropane and 25 ml of methanol were mixed. Further, 2 g of triethylamine and 1 ml of acetic acid were added thereto. The mixture was heated at reflux for 6 hours. The precipitated crystals were collected by filtration, washed with hot methanol and dried to obtain 6.9 g of Compound (IV-2). Melting Point: ≧300 °C.

$\lambda^{H_2O}_{max}$ = 493 nm, ϵ = 1.41 × 10^5

SYNTHESIS EXAMPLE IV-2

Compound (IV-9) of the Invention:

10.7 g of the sulfonated product of 1,2-diphenyl-3,5-pyrazolidinedione obtained in Synthesis Example IV-1, 2.8 g of 1-anilino-5-phenylimino-1,3-pentadiene hydrochloride and 4 ml of triethylamine were dissolved in 25 ml of methanol. 4.5 ml of acetic anhydride was added dropwise thereto at room temperature with stirring. The mixture was reacted for an additional 2 hours and the precipitated crystals were collected by filtration. The crude crystals were added to 50 ml of methanol and the mixture was heated to wash the crystals. The crystals were collected by filtration and dried to obtain 7.1 g of Compound (IV-9). Melting Point: ≧300 °C.

$\lambda^{H_2O}_{max}$ = 590 nm, ϵ = 1.80 × 10^5

SYNTHESIS EXAMPLE IV-3

Compound (IV-5) of the Invention:

Sodium Salt of 1-Phenyl-2-(2-sulfobenzyl)-3,5-pyrazolidinedione (Intermediate C)

104 g of phenylhydrazine was dissolved in 800 ml of methanol. A solution of 56 g of sodium o-formylbenzenesulfonate in 200 ml of methanol was added dropwise to the above solution at room temperature. With stirring, the mixture was heated at reflux for 2 hours. The mixture was then cooled and the resulting crystals were collected by filtration and washed with methanol to obtain 69 g of sodium 2-phenylhydrazonobenzenesulfonate (Intermediate A). 50 g of Intermediate A was dissolved in 250 ml of water and a palladiumcarbonic acid catalyst was added thereto. Intermediate A was hydrogenated in an autoclave. After the catalyst was separated by filtration, 250 ml of isopropanol was added thereto to thereby precipitate colorless crystals. The crystal were collected by filtration, washed with isopropanol and dried to obtain 43 g of sodium 2-phenylhydrazinobenzenesulfonate (Intermediate B). 40 g of Intermediate B, 19 g of diethyl malonate, 25 g of sodium methylate (28% methanol solution) and 100 ml of butanol were mixed and the mixture was heated at reflux for 10 hours. The n-butanol solution was concentrated and 200 ml of water was added to the residue. The aqueous layer was acidified with concentrated hydrochloric acid to precipitate crystals. The crystals were collected by filtration and washed with a small amount of methanol to obtain 39 g of Intermediate C.

7.4 g of sodium salt of 1-phenyl-2-(2-sulfobenzyl)-3,5-pyrazolidinedione was added to 50 ml of methanol. 4.2 ml of triethylamine and 2.5 g of malonaldehydodianil hydrochloride were then added thereto. The mixture was heated to prepare a uniform solution. After the solution was cooled to room temperature, 4.5 ml of acetic anhydride was added dropwise thereto. The mixture was reacted for 2 hours. 25 ml of isopropanol was then added thereto to thereby precipitate orange crystals. The crystals were collected by filtration, washed with isopropanol and dried to give 5 g of Compound (IV-5). Melting Point: ≧300 °C.

$\lambda^{H_2O}_{max}$ = 494 nm, ϵ = 1.32 × 10^5

When the dyes of the present invention are used as filter dyes, irradiation-preventing dyes or antihalation dyes, the dyes are used in such an amount that the desired results can be obtained. It is preferred that the dyes are used in an amount so as to give an optical density in the range of 0.05 to 3.0. The dyes may be added in any stage before coating.

The dyes of the present invention can be dispersed in emulsion layers and other hydrophilic colloid layers (e.g., an intermediate layer, a protective layer, an antihalation layer, a filter layer, etc.) using conventional methods.

For example, the dyes can be dispersed in these layers using the following methods.

(1) A method wherein the dyes of the present invention are directly dissolved in the emulsion layers or the hydrophilic colloid layers, or dispersed as fine particles in these layers. A method wherein the dyes are dissolved or dispersed as fine particles in an aqueous solution or a solution and the resulting solution or dispersion is applied to the emulsion layers and the hydrophilic colloid layers. Further, the dyes are dissolved in an appropriate solvent such as methyl alcohol, ethyl alcohol, propyl alcohol or methyl cellosolve and the solution added to emulsions. The dyes are dissolved in a solvent such as acetone, water, pyridine or a halogenated alcohol described in JP-A-48-9715 and U.S. Patent 3,756,830 or a mixed solvent thereof and the resulting solution added to emulsions.

(2) A method wherein hydrophilic polymers having a counter ion to the dye ion are present as mordants in the layers and the dyes are localized in specific layers due to an interaction between the polymer and the dye molecule.

Examples of the above-described polymer mordants are polymers having a secondary or tertiary amino group, polymers having a nitrogen-containing heterocyclic moiety and polymers having a quaternary cationic group. These polymers have a molecular weight of preferably 5,000 or higher, particularly preferably 10,000 or higher.

Specific examples of polymer mordants include vinylpyridine polymers and vinylpyridinium cation polymers as described in U.S. Patent 2,548,564; vinylimidazolium cation polymers as described in U.S Patent 4,124,386; polymer mordants capable of crosslinking with gelatin as described in U.S. Patent 3,625,694; aqueous sol type mordants as described in U.S. Patent 3,958,995 and JP-A-54-115228; water-insoluble mordants as described in U.S. Patent 3,989, 088; reactive mordants capable of forming a covalent bond to dyes as described in U.S. Patent 4,168,976; polymers derived from ethylenically unsaturated compounds having a residue of a dialkylaminoalkyl ester as described in British Patent 685,475; products obtained by reacting a polyvinyl alkyl ketone with an 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 wherein the compounds are dissolved in the presence of surfactants.

Useful surfactants may be oligomers or polymers.

Suitable polymers are fully described in JP-A-60-158437 (pages 19 to 27).

A hydrosol of a lipophilic polymer described in JP-B-51-39835 may be added to the hydrophilic colloid dispersion obtained as described above.

A typical example of a suitable hydrophilic colloid is gelatin. However, other hydrophilic colloid which are conventionally used in the field of photography can also be used.

Silver halide color photographic materials generally comprise three kinds of silver halide emulsion layers which are sensitized so as to be selectively sensitive to blue light, green light and red light, respectively. Each emulsion layer contains a coupler capable of reacting with the oxidation product of aromatic primary amine developing agents to form a dye. Generally, yellow, magenta and cyan colors, respectively, are formed. It is preferred that couplers have good color forming properties such that the coupling rate is as high as possible and they give a high color density within a restricted period of time. Further, it is required that color forming dyes scarcely give rise to any secondary absorption.

Further, it is required that the formed color images have good preservability under various conditions.

Suitable magenta couplers which meet these requirements include known couplers, which scarcely cause secondary absorption, as described in U.S. Patents 3,369,897 and 3,725,067, JP-A-59-162548, JP-A-59-171956, JP-A-59-228252, JP-A-60-33552, WO-86/1915 and JP-A-61-65245. Particularly, pyrazolone couplers have excellent color reproducibility with regard to red color and are practically used in the field of some color photographic materials.

Suitable yellow couplers are known couplers which have excellent color forming properties and have high activity as described in JP-A-60-229029.

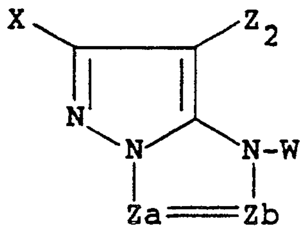
Suitable cyan couplers are known couplers as described in U.S. Patents 2,801,171, 2,895,826 and 3,772,002, JP-A-59-124341, JP-A-58-105229, JP-A-60-24547, JP-A-60-237448, JP-A-61-39045 and JP-A-61-77245.

Attempts have been made to apply these couplers directly to direct positive silver halide color photographic materials to utilize the excellent characteristics of these couplers.

In positive working silver halide photographic materials, however, it is necessary to increase the amount of silver to be coated because the ratio of the amount of silver developed to the coating silver weight is low as compared with negative type materials. Thus, problems exist in that the thickness of layer is increased and a harmful color due to dyes tends to be formed in the photographic materials after processing, that is, a dye color tends to remain in the photographic materials after processing.

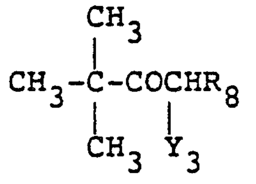
In a preferred embodiment of the present invention, the above-described dyes are used in combination with couplers which have good color forming properties and scarcely cause secondary absorption, whereby a positive silver halide color photographic material which has excellent sharpness and color reproducibility can be obtained.

Namely, in a preferred embodiment of the present invention, the silver halide color photographic material of the present invention contains at least one of each of a magenta coupler represented by the following formula (V), a yellow coupler represented by the following formula (VI) and a cyan coupler represented by the following formula (VII) or (VIII).



(V)

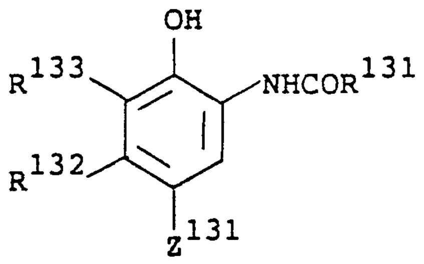
wherein X represents a hydrogen atom or a substituent group; Z_2 represents a hydrogen atom or a coupling elimination group (a group which is eliminated by coupling); W represents a hydrogen atom, an acyl group or an aliphatic or aromatic sulfonyl group; Za and Zb represent each a methine group, a substituted methine group or -N=; a dimer or polymer may be formed by X, Za or a substituted methine group of Za or Zb.



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CO\underset{Y_3}{C}HR_8}$$

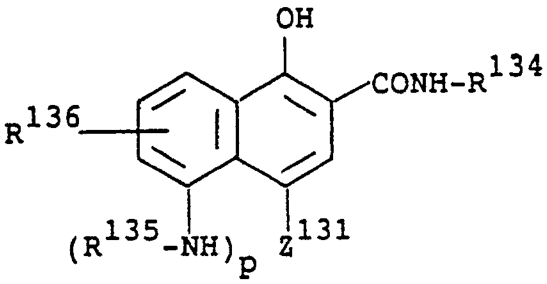
(VI)

wherein R_8 represents a substituted or unsubstituted N-phenylcarbamoyl group; Y_3 represents a group which is bonded through an oxygen atom or a nitrogen atom and is eliminated by the coupling reaction with the oxidation product of a primary amine color development agent.



(VII)

wherein R^{131} represents an alkyl group, an aryl group, an amino group or a heterocyclic group; R^{132} represents an acylamino group or an alkyl group; R^{133} represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; R^{133} and R^{132} may combine together to form a 5-membered to 7-membered ring; and Z'^{31} represents a hydrogen atom or a group which is eliminated by reaction with the oxidation product of an aromatic primary amine color developing agent.



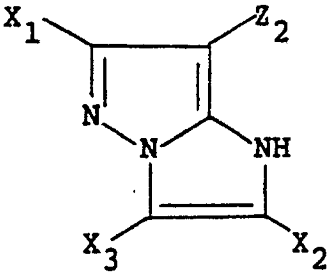
(VIII)

wherein R^{134} represents an alkyl group, an aryl group or a heterocyclic group; R^{135} represents an acyl group, a sulfonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group or an alkoxysulfonyl group; R^{136} represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an aryloxy group, an amido group, an imido group, an alkylthio group, an arylthio group, a ureido group, an alkylsulfonyl group or an arylsulfonyl group; p represents 0 or 1; and Z^{131} represents a hydrogen atom or a group which is eliminated by the reaction with the oxidation product of an aromatic primary amine developing agent.

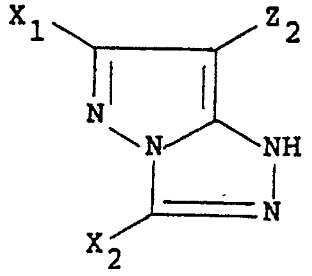
Magenta couplers having the formula (V) are illustrated in more detail below.

In the formula (V), the term "dimer or polymer" as used herein refers to compounds having at least 2 groups represented by the formula (V) per molecule. Accordingly, the term "dimer or polymer" includes bis compound couplers and polymer couplers. The polymer couplers may be homopolymers composed of a monomer having a moiety represented by the formula (V) (preferably a monomer having a vinyl group, hereinafter referred to as a vinyl monomer) or copolymers of this monomer with a non-color-forming ethylenic monomer which is not coupled with the oxidation product of aromatic primary amine color developing agents.

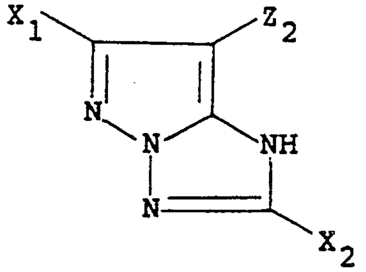
Of the pyrazoloazole couplers having the formula (V), the compounds represented by the following formulae (Va), (Vb), (Vc), (Vd) and (Ve) are preferred.



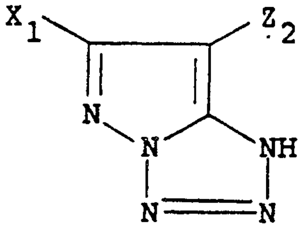
(Va)



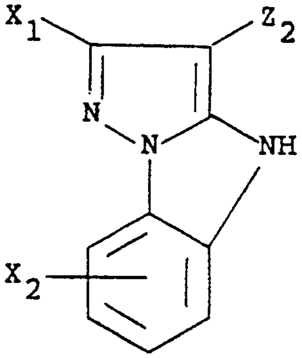
(Vb)



(Vc)



(Vd)



(Ve)

Of the couplers having the formulae (Va) to (Ve), the couplers having the formulae (Va), (Vb) and (Vc) are preferred. The couplers having the formula (Vc) are most preferred.

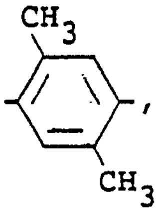
In the formulae (Va) to (Ve), X_1, X_2 and X_3, which may be the same or different, each is a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, a silyloxy group, a sulfonyloxy group, an acylamino group, an anilino group, a ureido group, an imido group, a sulfamoylamino group, a carbamoylamino group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonamido group, a carbamoyl group, an acyl group, a sulfamoyl group, a sulfonyl group, a sulfinyl group, an alkoxycarbonyl group or an aryloxycarbonyl group. These groups may be substituted. Groups described hereinafter also include substituted groups. Z_2 is a hydrogen atom, a halogen atom or a group which is bonded through an oxygen atom, a nitrogen atom or a sulfur atom to the carbon atom at the coupling position and is eliminated on coupling. X_1, X_2, X_3 or Z_2 may be a divalent group to form a bis compound.

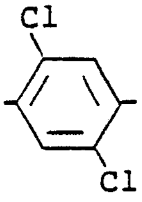
Couplers may be in the form of polymer couplers wherein the main chain comprises units composed of a residue of couplers having the formulae (Va) to (Ve) or polymers having side chains comprising units composed of a residue of the couplers having the formulae (Va) to (Ve). Polymers derived from a vinyl monomer with a moiety having the formula (Va), (Vb), (Vc), (Vd) or (Ve) are particularly preferred. In this case, X_1, X_2, X_3 or Z_2 is a vinyl group or a bonding group.

More specifically, X_1, X_2 and X_3 are each a hydrogen atom, a halogen atom (e.g., chlorine, bromine), an alkyl group (e.g., methyl, propyl, isopropyl, t-butyl, trifluoromethyl, tridecyl, 3-(2,4-di-t-amylphenoxy)propyl, 2-(2-octyloxy-5-t-octylbenzenesulfonamido)ethyl, allyl, 2-dodecyloxyethyl, 3-phenoxypropyl, 2-hexylsulfonylethyl, cyclopentyl, benzyl, etc.), an aryl group (e.g., phenyl, 4-t-butylphenyl, 2,4-di-t-amylphenyl, 4-tetradecanamidophenyl, etc.), a heterocyclic group (e.g., 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl, etc.), a cyano group, an alkoxy group (e.g., methoxy, ethoxy, 2-methoxyethoxy, isopropoxy, 2-dodecyloxyethoxy, 2-phenoxyethoxy, 2-methanesulfonylethoxy, etc.), an aryloxy group (e.g., phenoxy, 2-methylphenoxy, 2-methoxyphenoxy, 4-butylphenoxy, etc.), a heterocyclic oxy group (e.g., 2-benzimidazolyloxy, etc.), an acyloxy group (e.g., acetoxy, hexadecanoyloxy, etc.), a carbamoyloxy group (e.g., N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, etc.), a silyloxy group (e.g., trimethylsilyloxy, etc.), a sulfonyloxy group (e.g., dodecylsulfonyloxy, etc.), an acylamino group (e.g., acetamido, benzamido, tetradecanamido, α-(2,4-di-t-amylphenoxy)butyramido, γ-(3-t-butyl-4-hydroxyphenoxy)butyramido, α-[4-(4-hydroxyphenylsulfonyl)-phenoxy]decanamido, etc.), an anilino group (e.g., phenylamino, 2-chloroanilino, 2-chloro-5-tetradecanamidoanilino, 2-chloro-5-dodecyloxycarbonylanilino, N-acetylanilino, 2-chloro-5-[α-(3-t-butyl-4-hydroxyphenoxy)dodecanamido]anilino, etc.), a ureido group (e.g., phenylureido, methylureido, N,N-dibutylureido, etc.), an imido group (e.g., N-succinimido, 3-benzylhydantoinyl, 4-(2-ethylhexanoylamino)-phthalimido, etc.), a sulfamoylamino group (e.g., N,N-dipropylsulfamoylamino, N-methyl-N-decylsulfamoylamino, etc.), an alkylthio group (e.g., methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio, 3-(4-t-butylphenoxy)propylthio, etc.), an arylthio group (e.g., phenylthio, 2-butoxy-5-t-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio, 4-tetradecanamidophenylthio, etc.), a heterocyclic thio group (e.g., 2-benzothiozolylthio, etc.), an alkoxycarbonylamino group (e.g., methoxycarbonylamino, tetradecyloxycarbonylamino, etc.), an aryloxycarbonylamino group (e.g., phenoxycarbonylamino, 2,4-di-t-butylphenoxycarbonylamino, etc.), a sulfonamido group (e.g., methanesulfonamido, hexadecanesulfonamido, benzenesulfoamido, p-toluenesulfonamido, octadecanesulfonamido, 2-butyloxy-5-t-butylbenzenesulfonamido, etc.), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl, N-(2-dodecyloxyethyl)carbamoyl, N-methyl-N-dodecylcarbamoyl, N-[3-(2,4-di-t-amylphenoxy)propyl]carbamoyl, etc.), an acyl group (e.g., acetyl, (2,4-di-t-amylphenoxy)acetyl, benzoyl, etc.), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-(2-dodecyloxyethyl)sulfamoyl, N-ethyl-N-naphthoxy, 3-pentadecylphenoxy, benzyloxycarbonyloxy, ethoxy, 2-cyanoethoxy, benzyloxy, 2-phenethyloxy, 2-phenoxyethoxyhydantoinyl, 5-methyl-1-tetrazolyl, etc.), an arylazo group (e.g., 4-methoxyphenylazo, 4-pivaloylaminophenylazo, 2-naphthylazo, 3-methyl-4-hydroxyphenylazo, etc.), or a group which is bonded through a sulfur atom (e.g., phenylthio, 2-carboxyphenylthio, 2-methoxy-5-t-octylphenylthio, 4-methanesulfonylphenylthio, 4-octanesulfonamidophenylthio, 2-butoxyphenylthio, 2-(2-hexanesulfonylethyl)-5-t-octylphenylthio, benzylthio, 2-cyanoethylthio, 1-ethoxycarbonyltridecylthio, 5-phenyl-2,3,4,5-tetrazolylthio, 2-benzothiazolylthio, 2-dodecylthio-5-thiophenylthio, 2-phenyl-3-dodecyl-2,3,4-triazolyl-5-thio, etc.).

In the formula (Va), X_2 and X_3 may combine together to form a 5-membered to 7-membered ring.

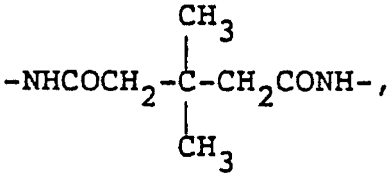
When X_1, X_2, X_3 or Z_2 is a divalent group to form a bis compound, X_1, X_2 and X_3 are each preferably a substituted or unsubstituted alkylene group (e.g., methylene, ethylene, 1,10-decylene, $-CH_2CH_2-O-CH_2CH_2-$, etc.), a substituted or unsubstituted phenylene group (e.g., 1,4-phenylene, 1,3-phenylene,



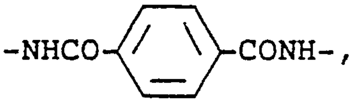
,


,

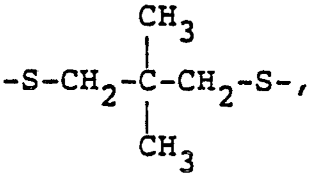
etc.), an -NHCO-X_4-CONH group (wherein X_4 is a substituted or unsubstituted alkylene or phenylene group, such as -NHCOCH$_2$CH$_2$CONH-,



$$-NHCOCH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CONH-,$$



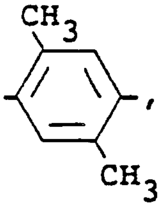
etc.), or an -S-X$_5$-S- group (wherein X$_5$ is a substituted or unsubstituted alkylene group, such as -S-CH$_2$CH$_2$-S-,

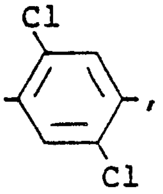


$$-S-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-S-,$$

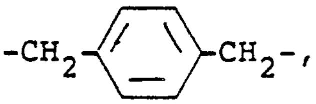
etc.), and Z$_2$ is a divalent group derived from a member selected from the monovalent groups described above for Z$_2$.

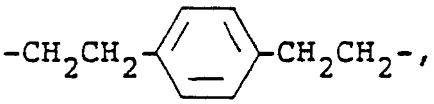
When the compounds having the formulae (Va), (Vb), (Vc), (Vd) and (Ve) are each a moiety of a vinyl monomer, the bonding group represented by X$_1$, X$_2$, X$_3$ or Z$_2$ is a group selected from the group consisting of a substituted or unsubstituted alkylene group (e.g., methylene, ethylene, 1,10-decylene, -CH$_2$CH$_2$OCH$_2$CH$_2$-, etc.), a substituted or unsubstituted phenylene group (e.g., 1,4-phenylene, 1,3-phenylene,

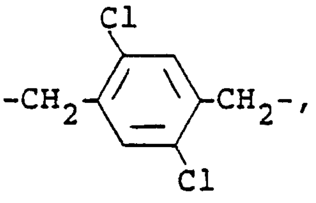




etc.), -NHCO-, -CONH-, -O-, -OCO-, and an aralkylene group (e.g.,

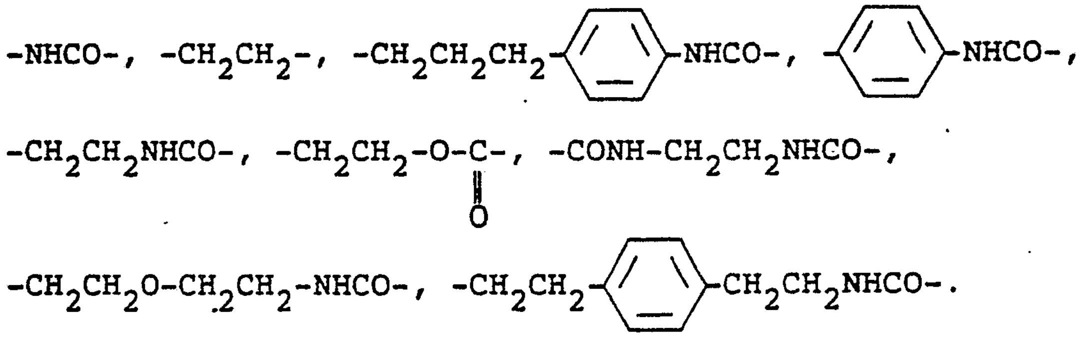






etc.), or a combination thereof.

Preferred examples of bonding groups are the following groups:



A vinyl group may have one or more substituent groups in addition to the moiety represented by the formula (Va), (Vb), (Vc), (Vd) or (Ve). Preferred substituent groups are a chlorine atom and a lower alkyl group having from 1 to 4 carbon atoms (e.g., methyl, ethyl).

Monomers containing a moiety represented by the formula (Va), (Vb), (Vc), (Vd) or (Ve) may be copolymerized with non-color-forming ethylenic monomers which do not couple with the oxidation product of aromatic primary amine developing agents to form copolymers.

Examples of non-color-forming ethylenic monomers which do not couple with the oxidation product of aromatic primary amine developing agents include acrylic acid, α-chloroacrylic acid, α-alkylacrylic acid (e.g., methacrylic acid) and esters and amides derived from these acrylic acids (e.g., acrylamide, n-butylacrylamide, t-butylacrylamide, diacetone acrylamide, methacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and β-hydroxy methacrylate), methylenedibisacrylamide, vinyl esters (e.g., vinyl acetate, vinyl propionate and vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (e.g., styrene and derivatives thereof, vinyltoluene, divinylbenzene, vinylacetophenone and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers (e.g., vinyl ethyl ether), maleic acid, maleic anhydride, maleates, N-vinyl-2-pyrrolidone, N-vinylpyridine and 2- and 4-vinylpyridine. These non-color-forming ethylenically unsaturated monomers may be used either alone or as a combination of two or more of them. For example, a combination of n-butyl acrylate and methyl acrylate, a combination of styrene and methacrylic acid, a combination of methacrylic acid and acrylamide and a combination of methyl acrylate and diacetone acrylamide can be used.

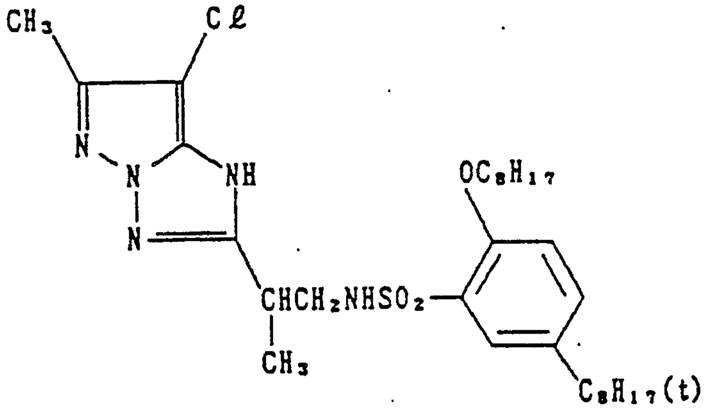
The ethylenically unsaturated monomers to be copolymerized with the solid water-insoluble monomer couplers can be chosen so as to provide copolymers having good physical properties and/or chemical properties such as solubility, compatibility with binders (e.g., gelatin) in photographic colloid compositions, flexibility, thermal stability, etc., well known in the field of polymer color couplers.

The polymer couplers which are used in the present invention may be water-soluble or water-insoluble. Among them, polymer coupler latexes are particularly preferred.

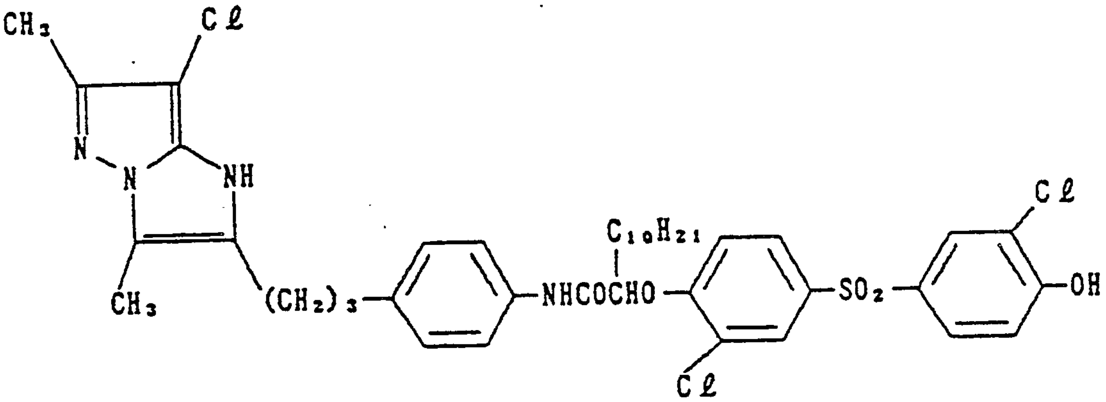
These couplers can be synthesized by the methods described in JP-A-59-171596, JP-A-60-172982, JP-A-60-190779, JP-A-60-197688 and JP-A-60-215687.

Examples of magenta couplers which can be used in the present invention include, but are not limited to, the following compounds.

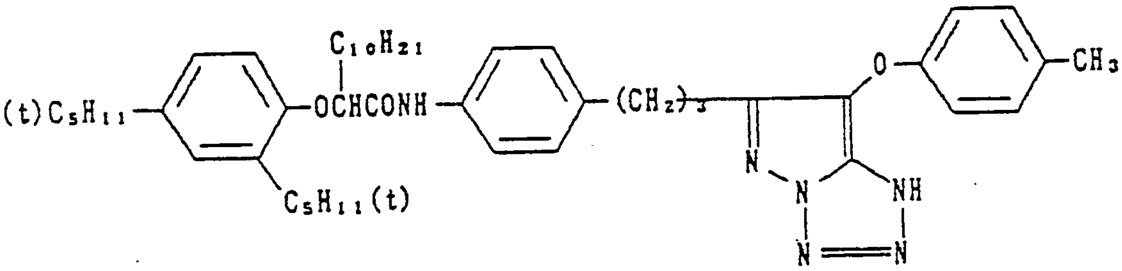
(M－1)


CH3
Cℓ
N
N
NH
N
OC8H17
CHCH2NHSO2
CH3
C8H17(t)

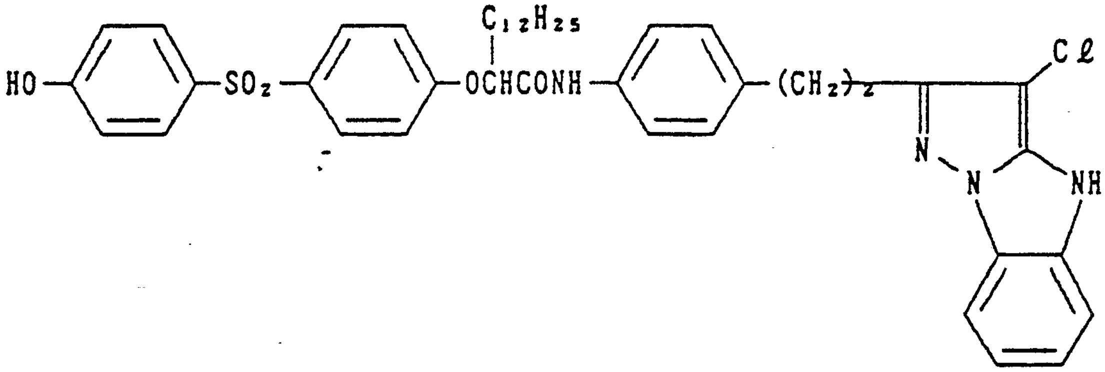
(M－2)


CH3
Cℓ
N
N
NH
CH3
(CH2)3
NHCOCHO
C10H21
SO2
Cℓ
OH
Cℓ

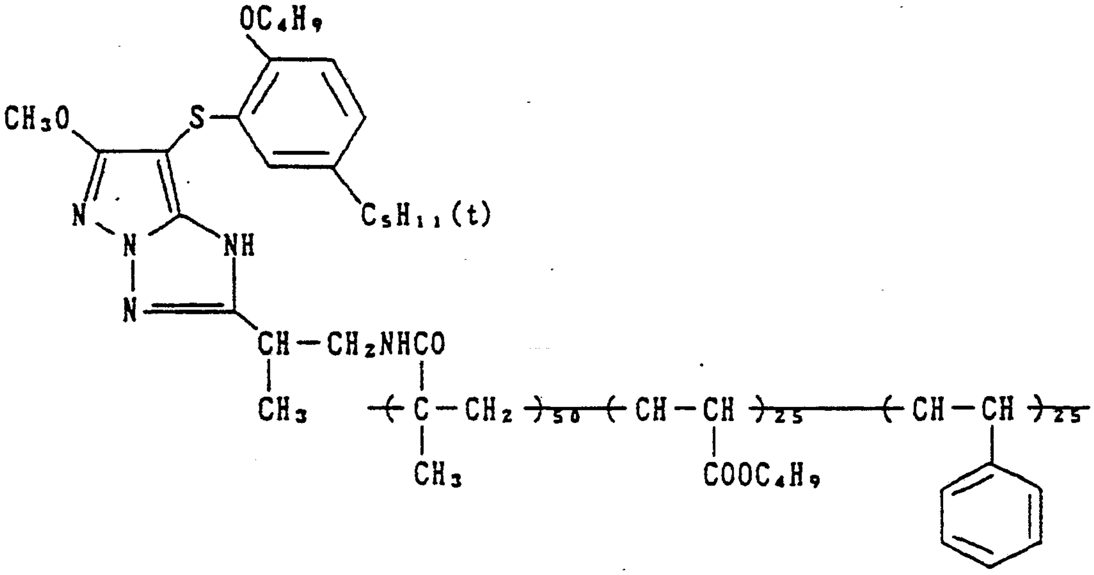
(M－3)


(t)C5H11
C10H21
OCHCONH
C5H11(t)
(CH2)3
O
CH3
N
N
NH
N
N

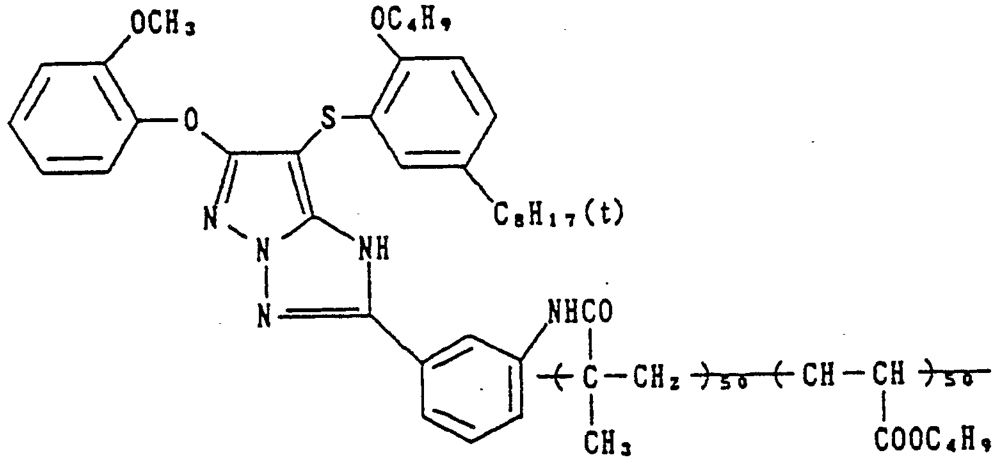
(M－4)



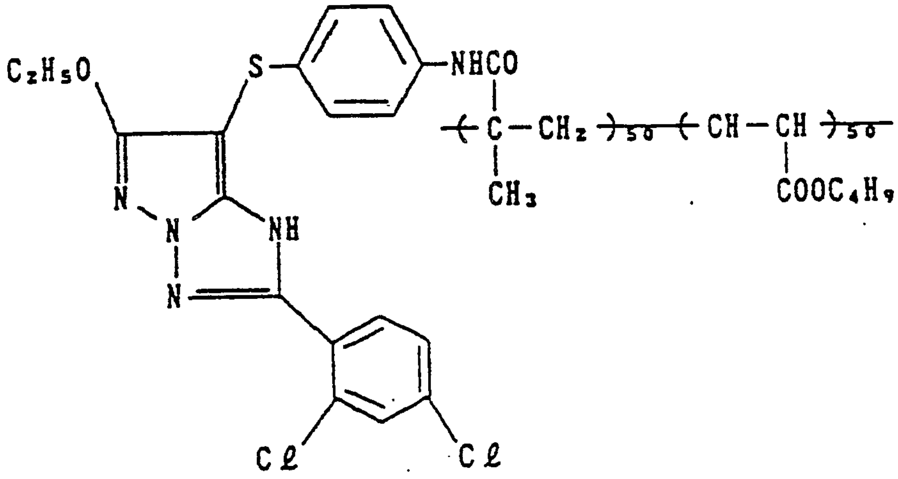
(M－5)



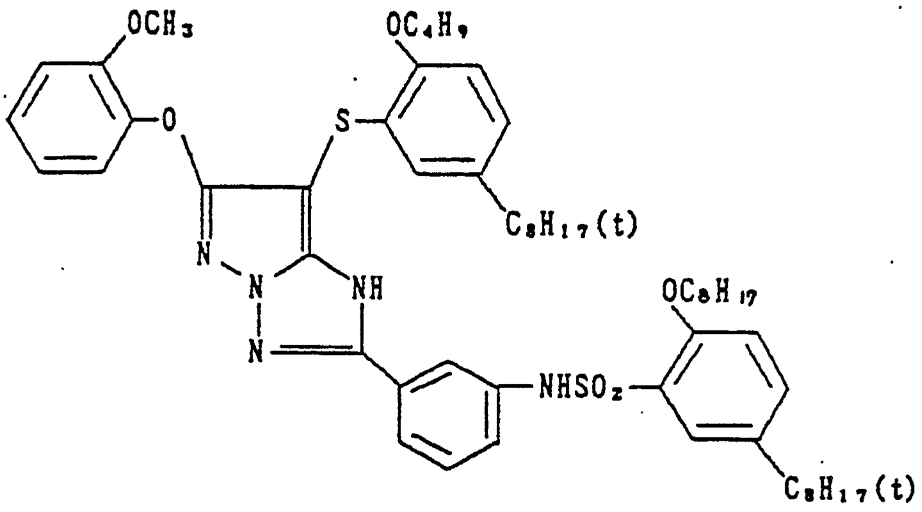
(M－6)


OCH₃
OC₄H₉
O
S
C₈H₁₇(t)
N
N
NH
N
NHCO
⟵C—CH₂⟶₅₀⟵CH—CH⟶₅₀
CH₃
COOC₄H₉

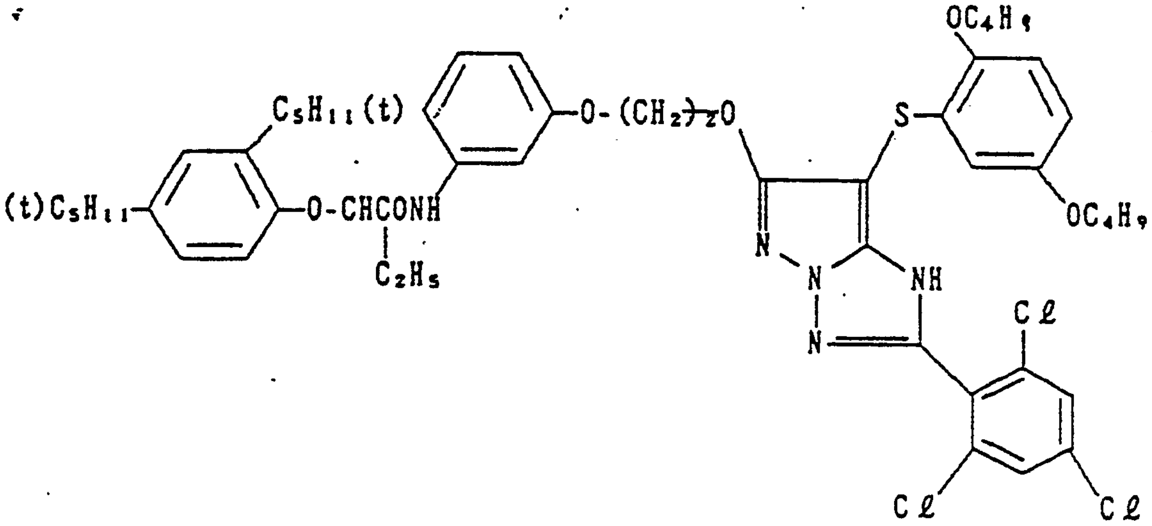
(M－7)


C₂H₅O
S
NHCO
⟵C—CH₂⟶₅₀⟵CH—CH⟶₅₀
CH₃
COOC₄H₉
N
N
NH
N
Cℓ
Cℓ

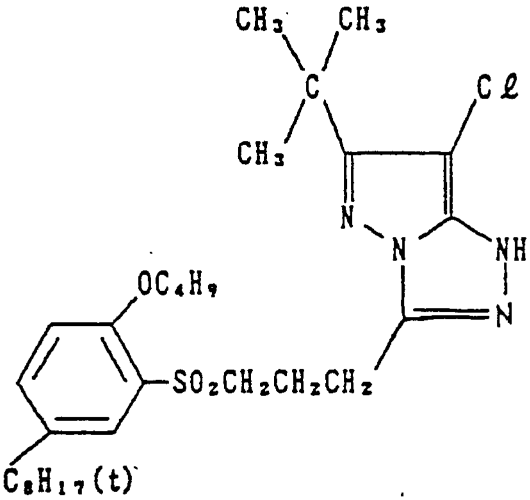
(M－8)


OCH3
OC4H9
O
S
C8H17(t)
N
N
NH
N
OC8H17
NHSO2
C8H17(t)

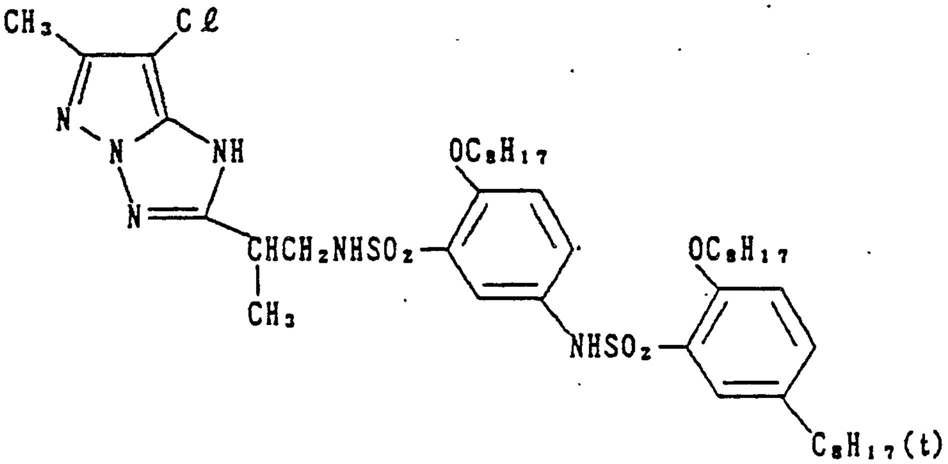
(M－9)


OC4H9
C5H11(t)
O-(CH2)2O
S
(t)C5H11
O-CHCONH
C2H5
OC4H9
N
N
NH
N
Cℓ
Cℓ
Cℓ

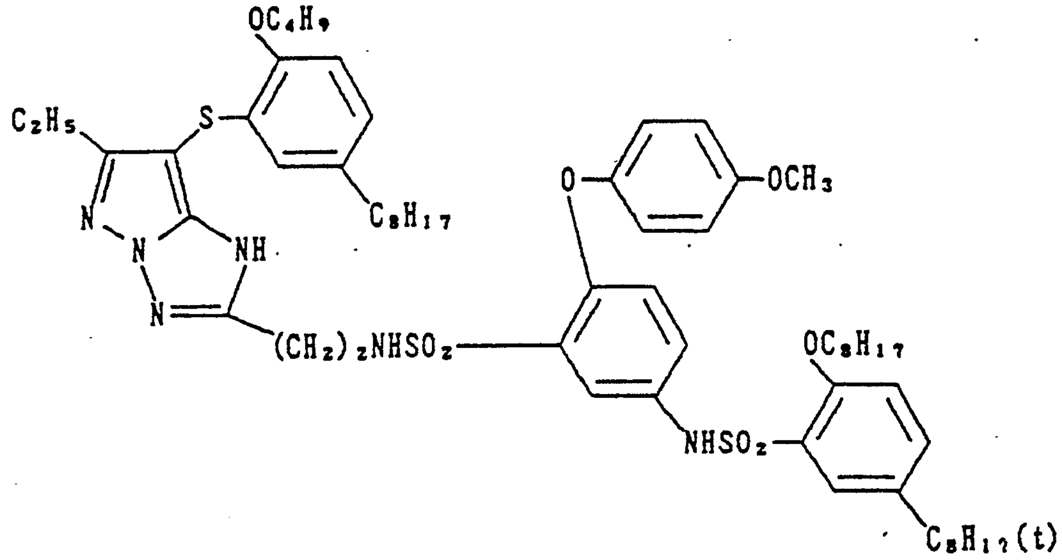
(M－10)


CH₃
CH₃
C
CH₃
Cℓ
N
N
NH
N
OC₄H₉
SO₂CH₂CH₂CH₂
C₈H₁₇(t)

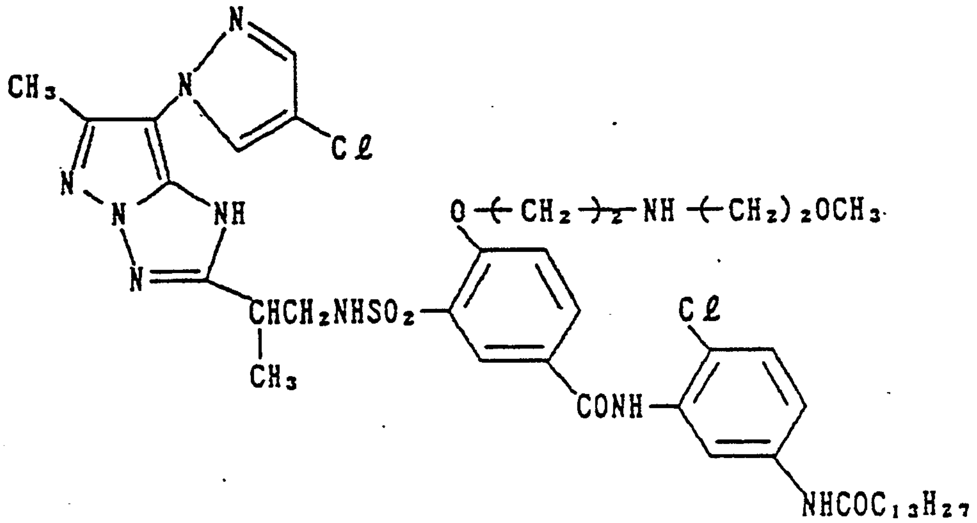
(M－11)


CH₃
Cℓ
N
N
NH
N
CHCH₂NHSO₂
CH₃
OC₈H₁₇
NHSO₂
OC₈H₁₇
C₈H₁₇(t)

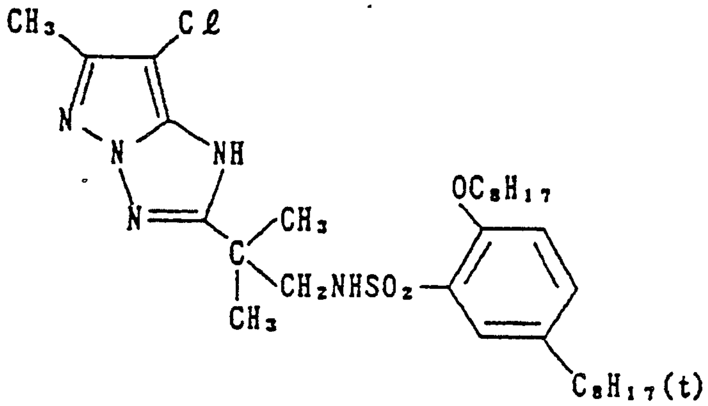
(M－12)


OC4H9
C2H5
S
O
OCH3
C8H17
N
N
NH
N
(CH2)2NHSO2
OC8H17
NHSO2
C8H17(t)

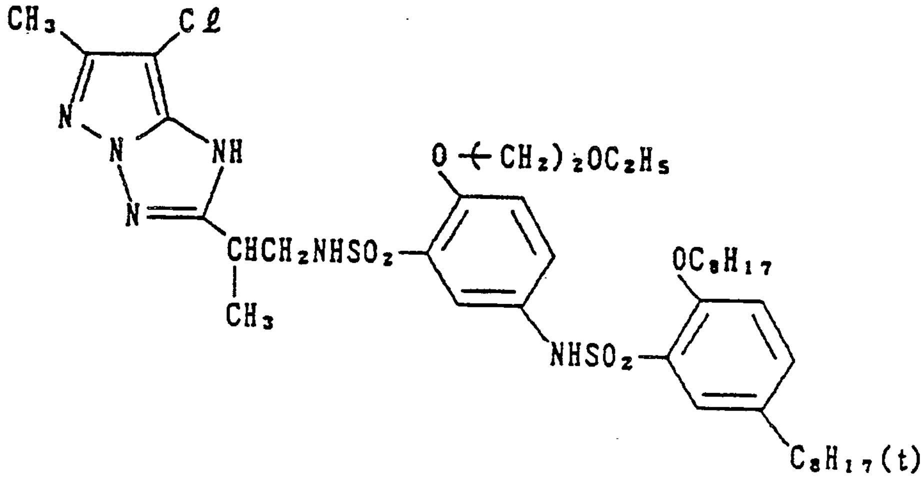
(M－13)


N
CH3
N
Cℓ
N
N
NH
O ⟵CH2⟶2 NH ⟵CH2)2OCH3
N
CHCH2NHSO2
CH3
Cℓ
CONH
NHCOC13H27

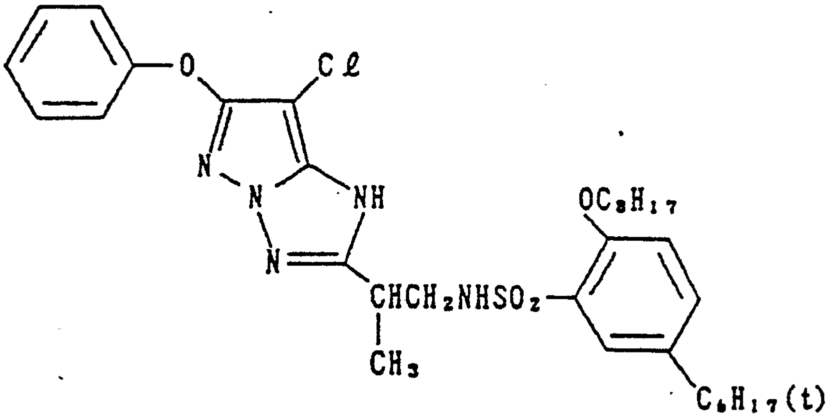
(M−14)


CH3
Cℓ
N
N
NH
N
CH3
C
CH2NHSO2
CH3
OC8H17
C8H17(t)

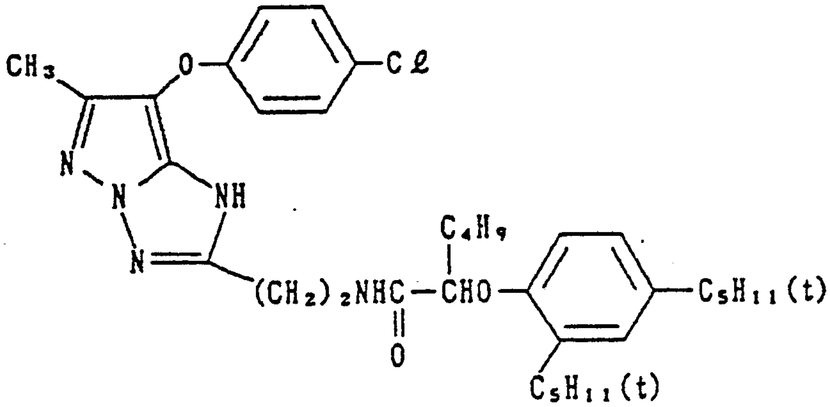
(M−15)


CH3
Cℓ
N
N
NH
N
CHCH2NHSO2
CH3
O ⟵CH2)2OC2H5
NHSO2
OC8H17
C8H17(t)

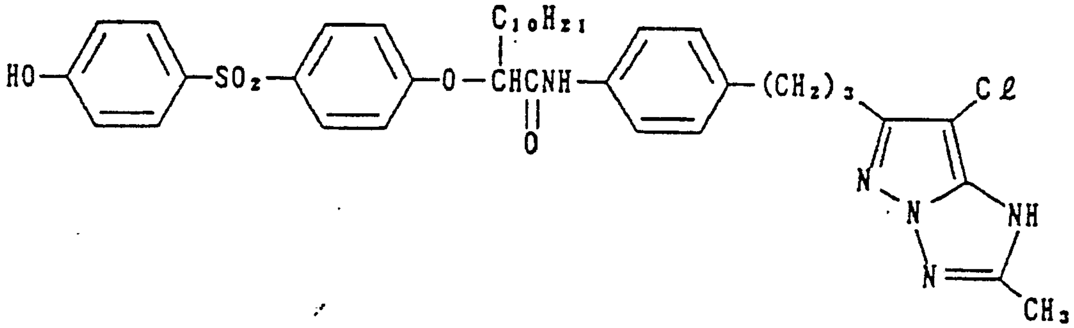
(M－16)


Cℓ
O
N
N
NH
N
OC8H17
CHCH2NHSO2
CH3
C8H17(t)

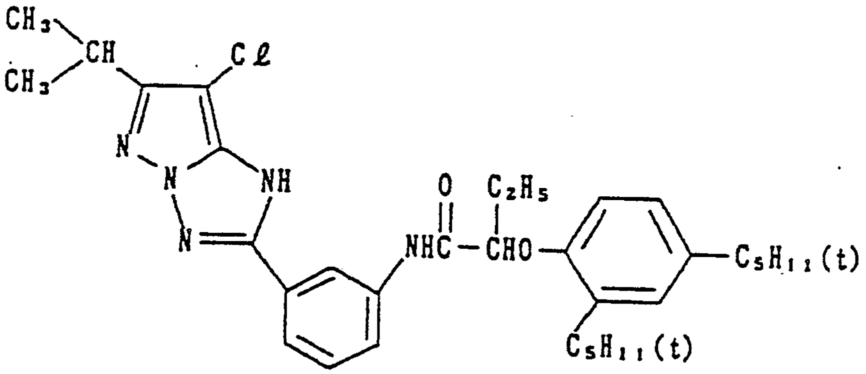
(M－17)


CH3
O
Cℓ
N
N
NH
N
C4H9
(CH2)2NHC
CHO
O
C5H11(t)
C5H11(t)

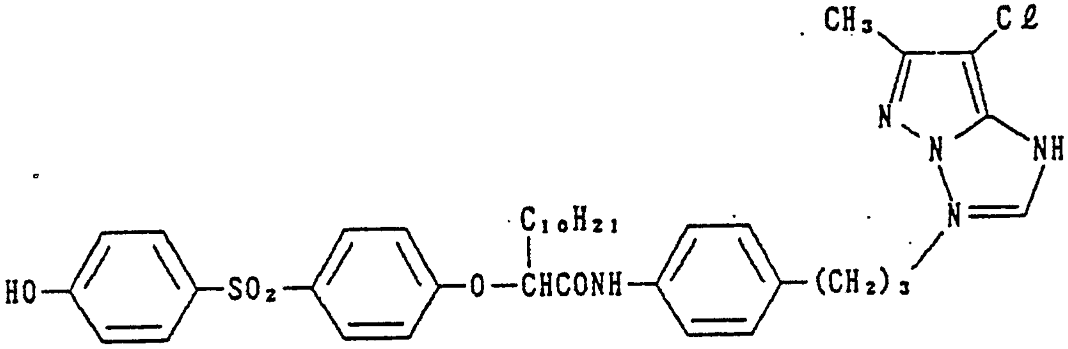
(M－18)


HO
SO₂
O
C₁₀H₂₁
CHCNH
O
(CH₂)₃
Cℓ
N
N
NH
N
CH₃

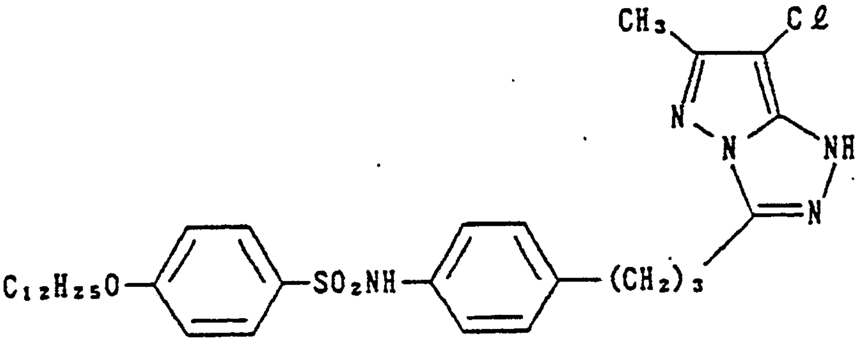
(M－19)


CH₃
CH
CH₃
Cℓ
N
N
NH
N
O
C₂H₅
NHC
CHO
C₅H₁₁(t)
C₅H₁₁(t)

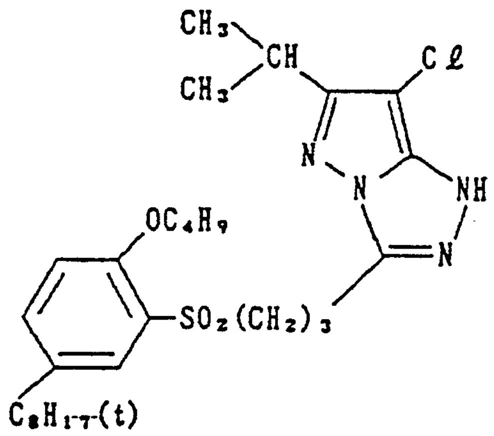
(M－２０)


CH₃
Cℓ
N
N
NH
N
C₁₀H₂₁
HO
SO₂
O
CHCONH
(CH₂)₃

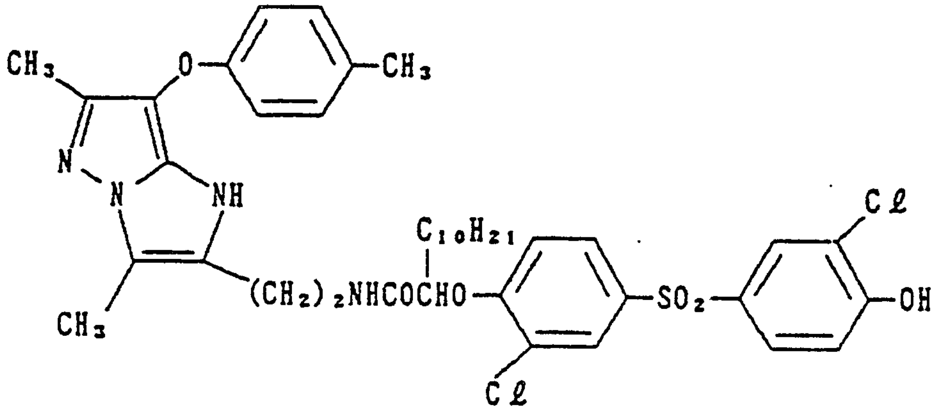
(M－２１)


CH₃
Cℓ
N
N
NH
N
C₁₂H₂₅O
SO₂NH
(CH₂)₃

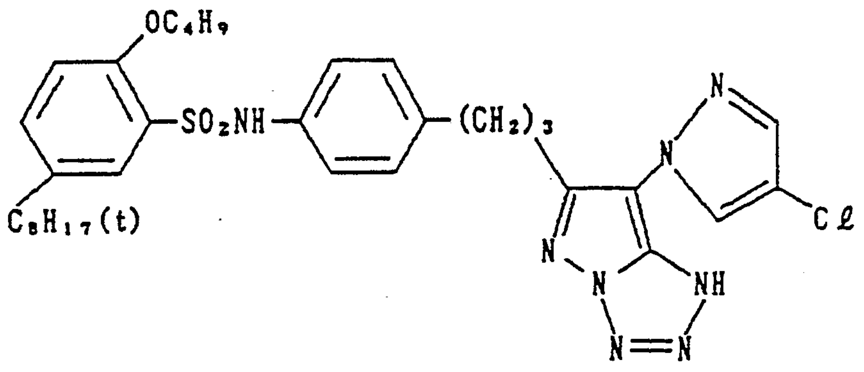
(M－22)


CH₃
CH
CH₃
Cℓ
N
N
NH
N
OC₄H₉
SO₂(CH₂)₃
C₈H₁₇-(t)

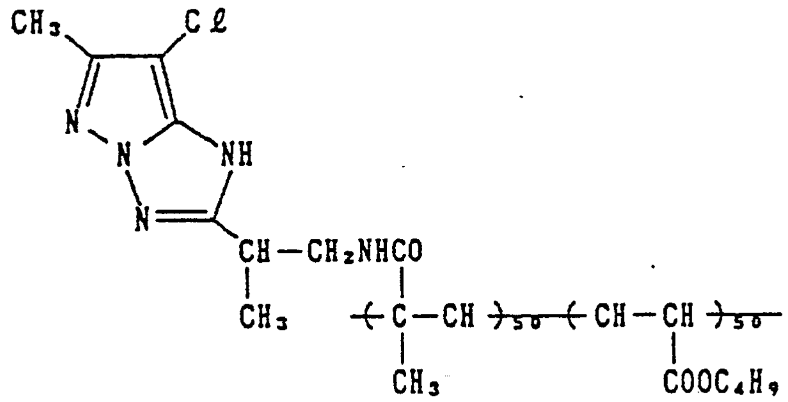
(M－23)


CH₃
O
CH₃
N
N
NH
CH₃
C₁₀H₂₁
(CH₂)₂NHCOCHO
SO₂
Cℓ
OH
Cℓ

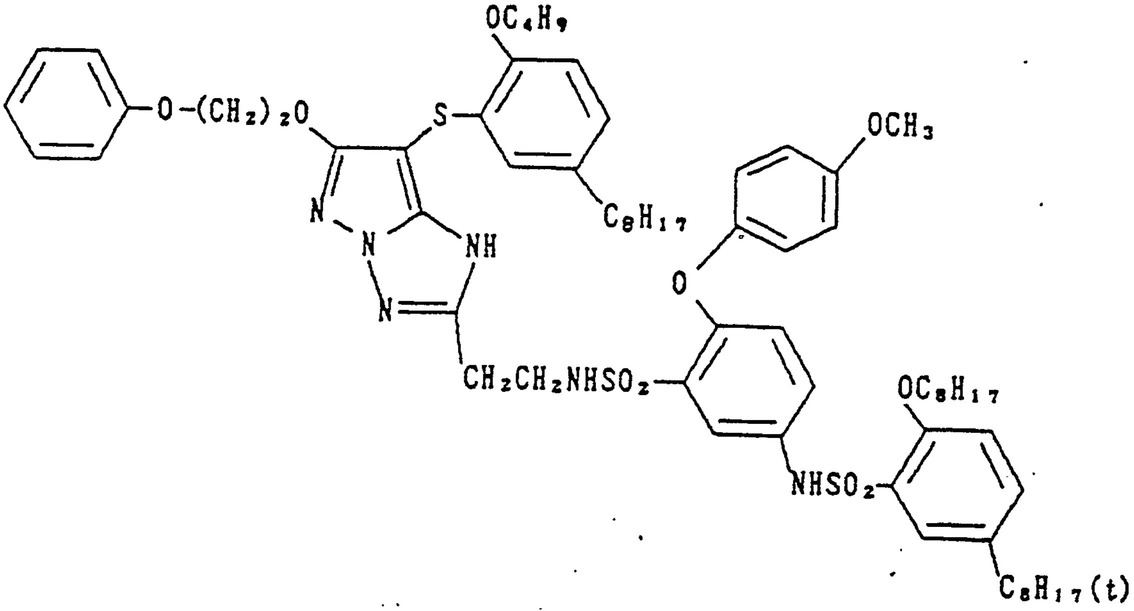
(M－２４)



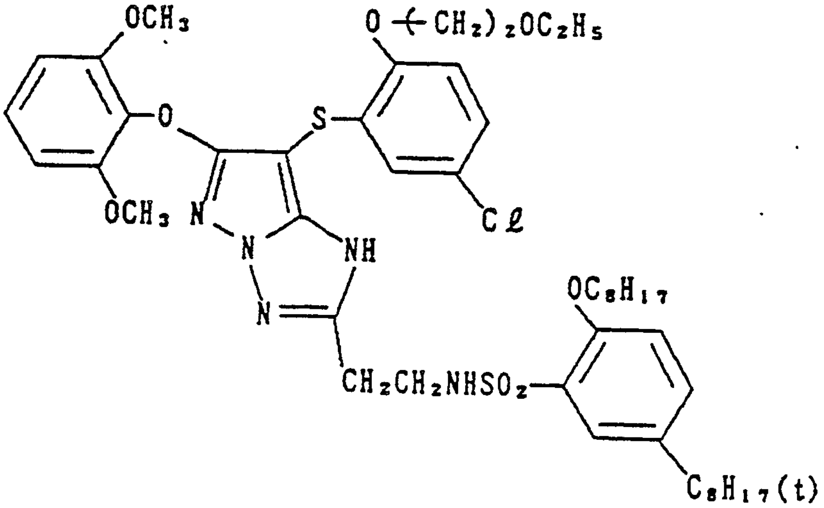
(M－２５)



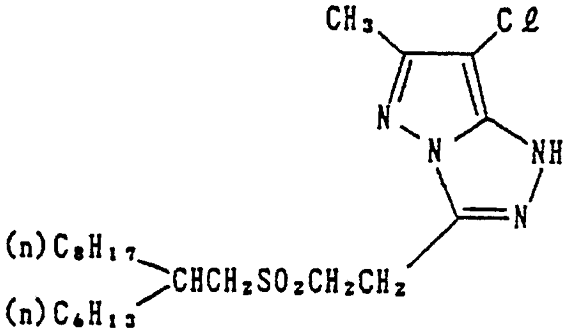
(M－２６)


OC₄H₉
O-(CH₂)₂O
S
OCH₃
N
N
NH
C₈H₁₇
O
N
CH₂CH₂NHSO₂
OC₈H₁₇
NHSO₂
C₈H₁₇(t)

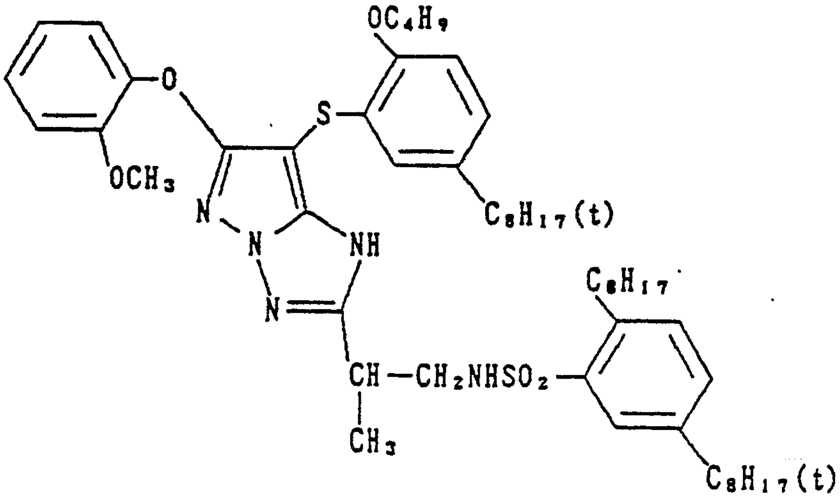
(M－２７)


OCH₃
O ⟵CH₂)₂OC₂H₅
O
S
OCH₃
N
N
NH
Cℓ
N
OC₈H₁₇
CH₂CH₂NHSO₂
C₈H₁₇(t)

(M-28)



(M-29)



Couplers having the formula (V) can be synthesized according to the methods described in U.S. Patents 3,369,897 and 3,725,067, JP-A-59-162548, JP-A-59-171956, JP-A-59-228252, JP-A-60-33552, WO 86/1915 and JP-A-61-65245 and similar methods.

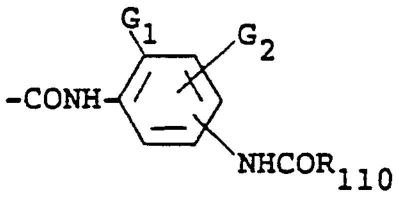
These couplers of the formula (V) are used in an amount of 1×10^{-3} to 1 mol, preferably 5×10^{-2} to 5×10^{-1} mol, per mol of silver halide in the emulsions.

Yellow couplers represented by the formula (VI) are illustrated in greater detail below.

In the formula (VI), R_8 is an N-phenylcarbamoyl group. The phenyl group may optionally have one or more substituent groups. When two or more substituent groups are present, they may be the same or different groups.

Examples of suitable substituent groups which can be used include an aromatic group (e.g., phenyl, naphthyl), a heterocyclic group (e.g., 2-pyridyl, 2-imidazolyl, 2-furyl, 6-quinolyl, etc.), an aliphatic oxy group (e.g., methoxy, 2-methoxyethoxy, 2-propenyloxy, etc.), an aromatic oxy group (e.g., 2,4-di-tert-amylphenoxy, 4-cyanophenoxy, 2-chlorophenoxy, etc.), an acyl group (e.g., acetyl, benzoyl, etc.), an ester group (e.g., butoxycarbonyl, phenoxycarbonyl, acetoxy, benzoyloxy, butoxysulfonyl, toluenesulfonyloxy, etc.), an amido group (e.g., acetylamino, methanesulfonamido, ethylcarbamoyl, butylsulfamoyl, etc.), an imido group (e.g., succinimido, hydantoinyl, etc.), a ureido group (e.g., phenylureido, dimethylureido, etc.), an aliphatic or aromatic sulfonyl group (e.g., methanesulfonyl, phenylsulfonyl, etc.), an aliphatic or aromatic thio group (e.g., phenylthio, ethylthio, etc.), a hydroxyl group, a cyano group, a carboxyl group, a nitro group, a sulfo group and a halogen atom (e.g., fluorine, chlorine, bromine, etc.).

Preferably, R_8 is a group represented by the following formula (A):



(A)

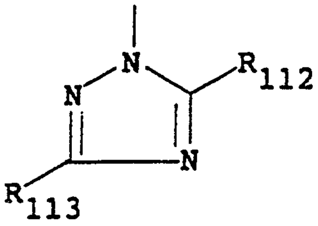
wherein G_1 is a halogen atom or an alkoxy group; G_2 is a hydrogen atom or an alkoxy group which may be optionally substituted; and R_{110} is an alkyl group which may be optionally substituted.

Examples of substituent groups for G_2 and R_{110} in the formula (A) include an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group, a dialkylamino group, a heterocyclic group (e.g., N-morpholino, N-piperidino, 2-furyl, etc.), halogen, a nitro group, a hydroxyl group, a carboxyl group, a sulfo group and an alkoxycarbonyl group.

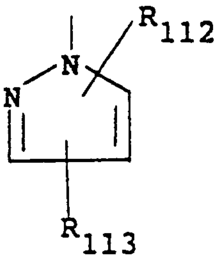
Y_3 is a group which is eliminated. Preferably, Y_3 is a group selected from groups represented by the following formulae (B) to (E):

$-OR_{111}$ (B)

wherein R_{111} is a substituted or unsubstituted aryl or heterocyclic group;

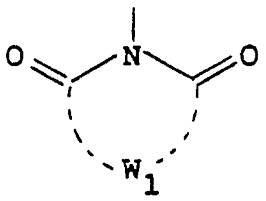


(C)



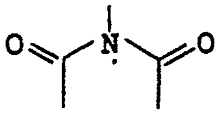
(D)

wherein R_{112} and R_{113} are each a hydrogen atom, a halogen atom, a carboxylic ester group, an amino group, an alkyl group, an alkylthio group, an alkoxy group, an alkylsulfonyl group, an alkylsulfinyl group, a carboxyl group, a sulfo group, an unsubstituted or substituted phenyl group or an unsubstituted or substituted heterocyclic group and R_{112} and R_{113} may be the same or different groups;

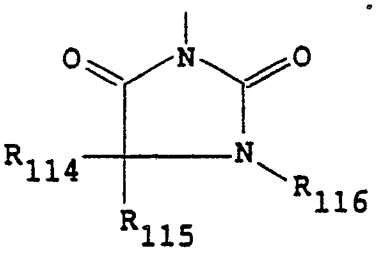


(E)

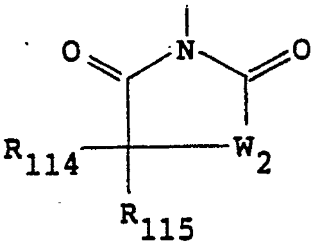
wherein W_1 is a nonmetallic atomic group required for the formation of a 4-membered, 5-membered or 6-membered ring together with



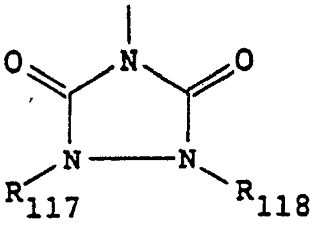
Of the groups of the formula (E), the groups represented by the following formulae (E-1) to (E-3) are preferred.



(E-1)



(E-2)



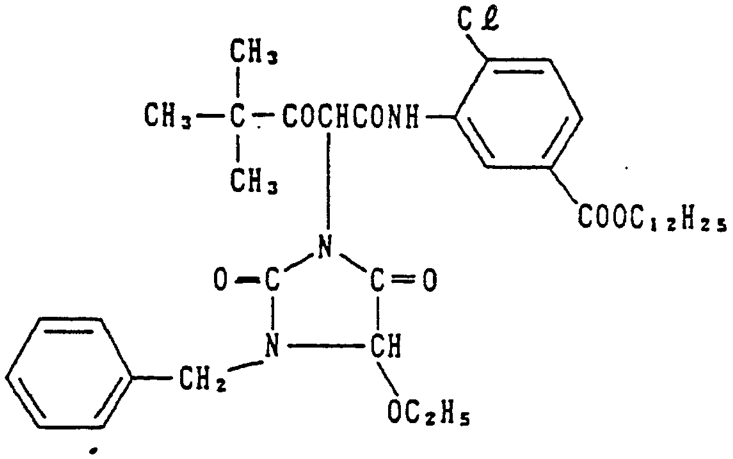
(E-3)

wherein R_{114} and R_{115} are each a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group or a hydroxyl group; R_{116}, R_{117} and R_{118} are each a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or an acyl group; and W_2 is an oxygen atom or a sulfur atom.

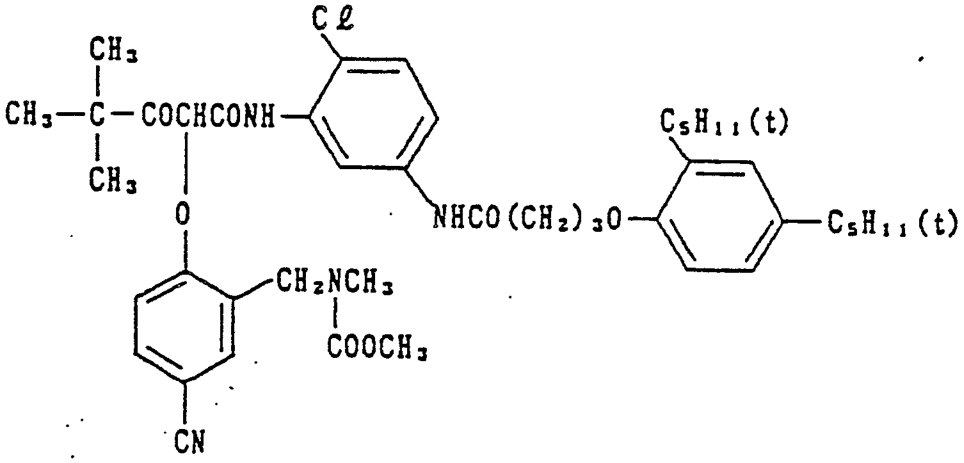
The alkyl moiety and the aryl moiety in the groups represented by the above formulae may be optionally substituted by the substituent groups already described above.

Examples of suitable yellow couplers which can be used in the present invention include, but are not limited to, the following compounds.

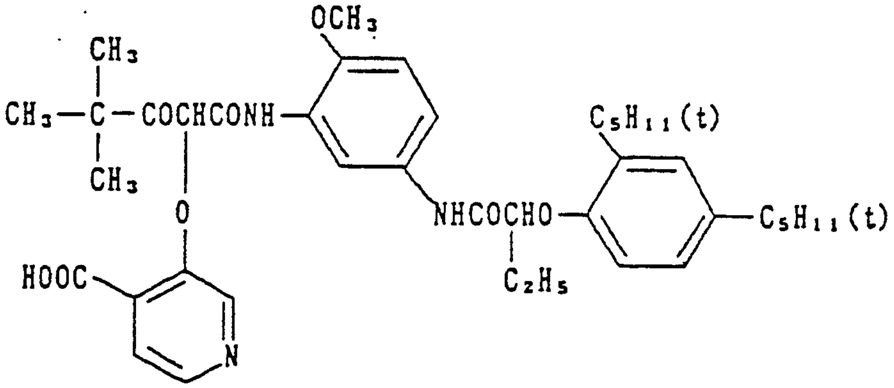
(Y－1)


Cℓ
CH₃
CH₃—C—COCHCONH
CH₃
COOC₁₂H₂₅
N
O=C
C=O
N
CH
CH₂
OC₂H₅

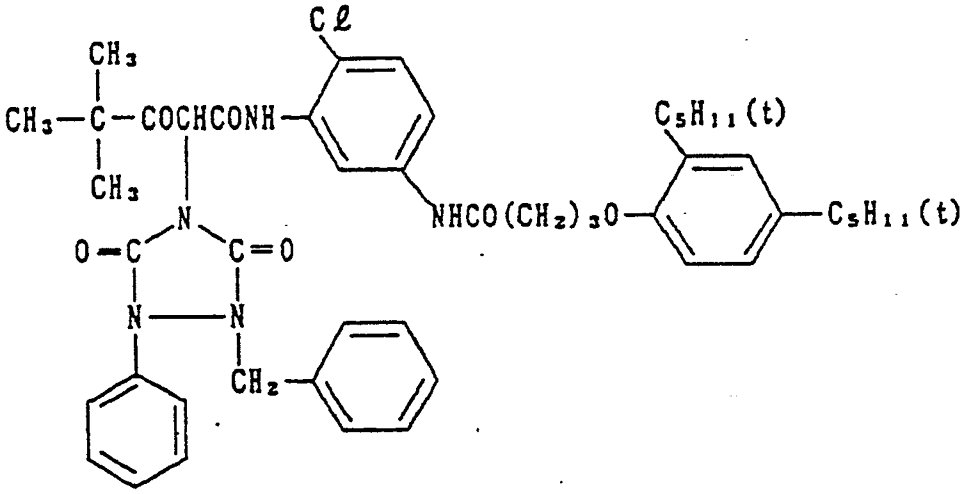
(Y－2)


Cℓ
CH₃
CH₃—C—COCHCONH
CH₃
O
C₅H₁₁(t)
NHCO(CH₂)₃O
C₅H₁₁(t)
CH₂NCH₃
COOCH₃
CN

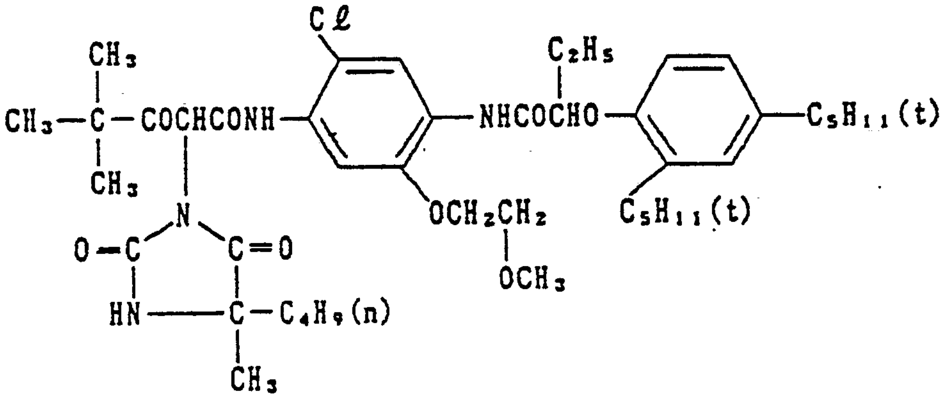
(Y－3)


OCH₃
CH₃
CH₃—C—COCHCONH
CH₃
O
C₅H₁₁(t)
NHCOCHO
C₂H₅
C₅H₁₁(t)
HOOC
N

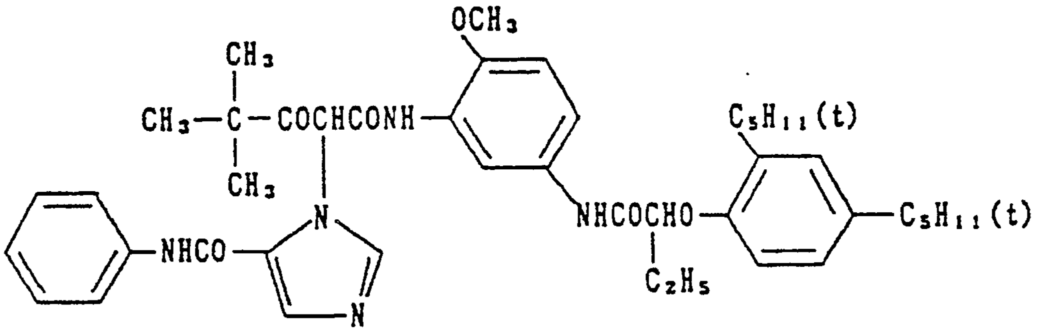
(Y－4)



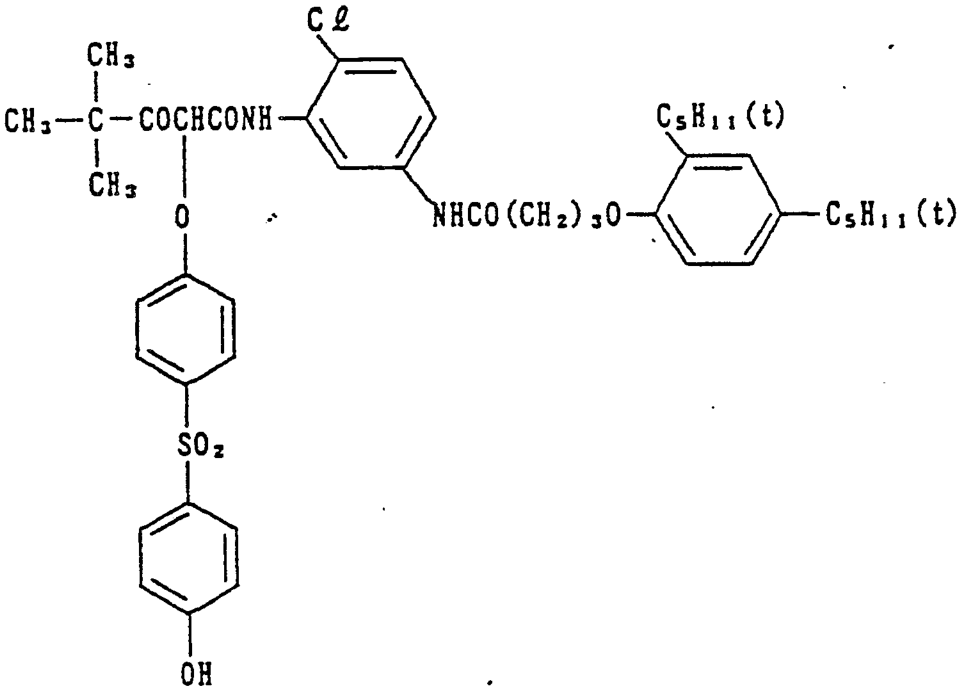
(Y－5)



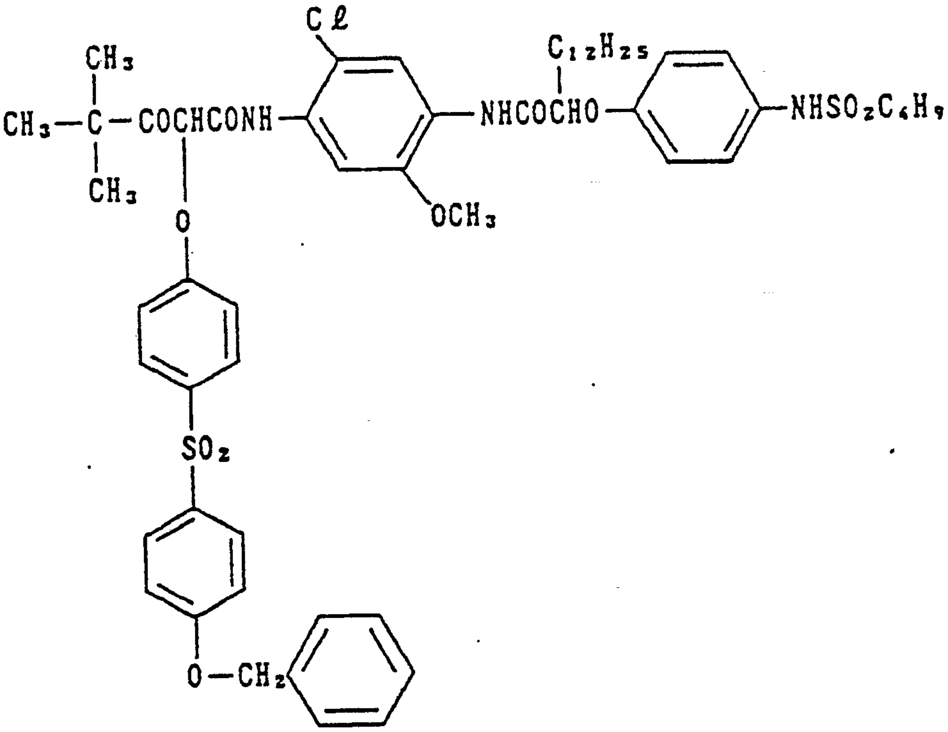
(Y－6)


OCH3
CH3
CH3—C—COCHCONH—
CH3
N
N
NHCO
NHCOCHO
C2H5
C5H11(t)
C5H11(t)

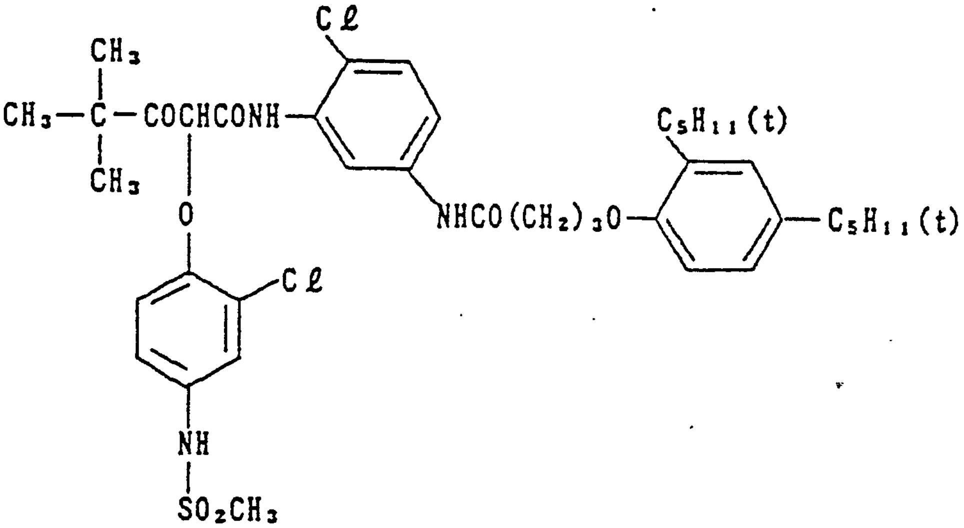
(Y－7)


Cℓ
CH3
CH3—C—COCHCONH—
CH3
O
NHCO(CH2)3O
C5H11(t)
C5H11(t)
SO2
OH

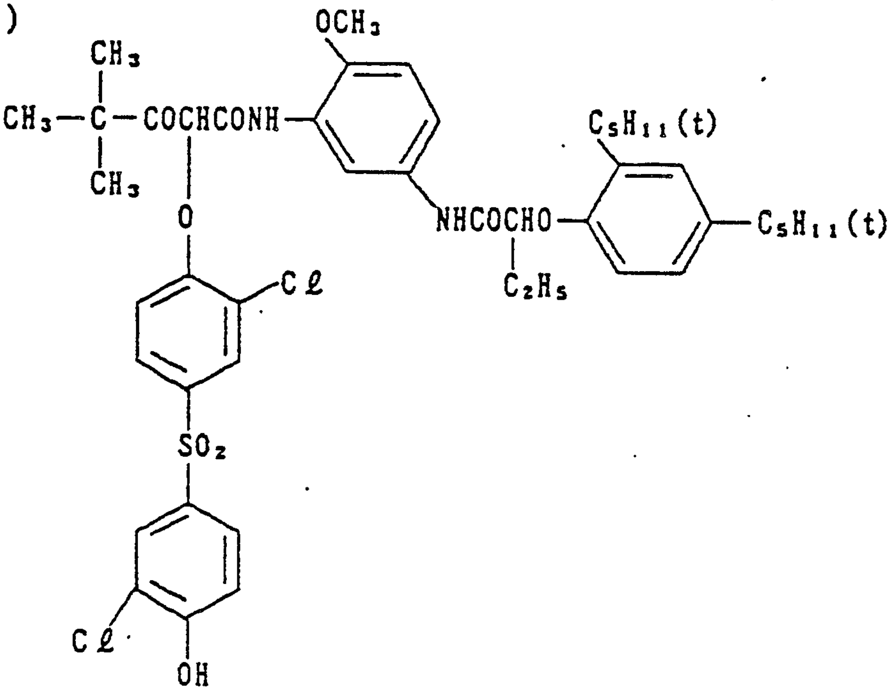
(Y－8)


Cℓ
CH₃
CH₃—C—COCHCONH
CH₃
O
C₁₂H₂₅
NHCOCHO
NHSO₂C₄H₉
OCH₃
SO₂
O—CH₂

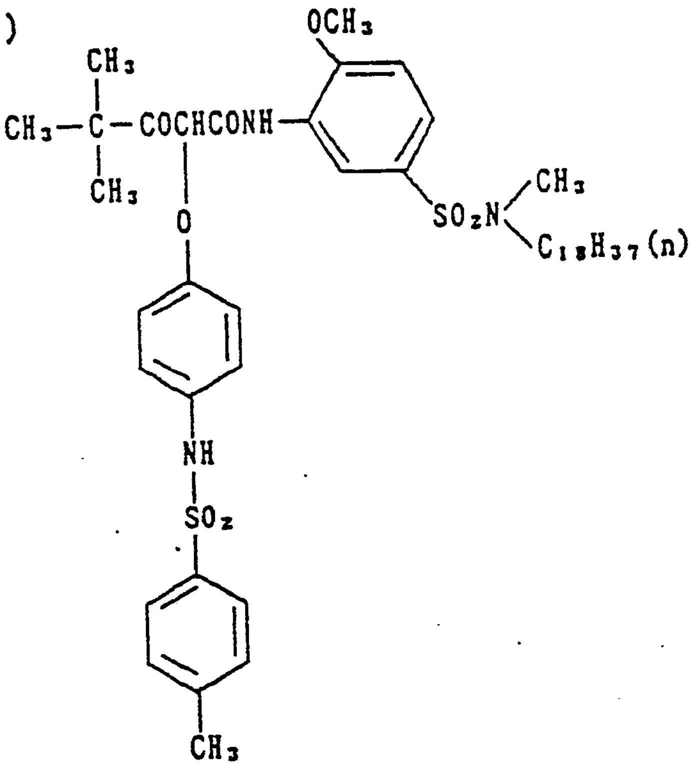
(Y－9)


Cℓ
CH₃
CH₃—C—COCHCONH—
CH₃
O
Cℓ
NH
SO₂CH₃
NHCO(CH₂)₃O—
C₅H₁₁(t)
—C₅H₁₁(t)

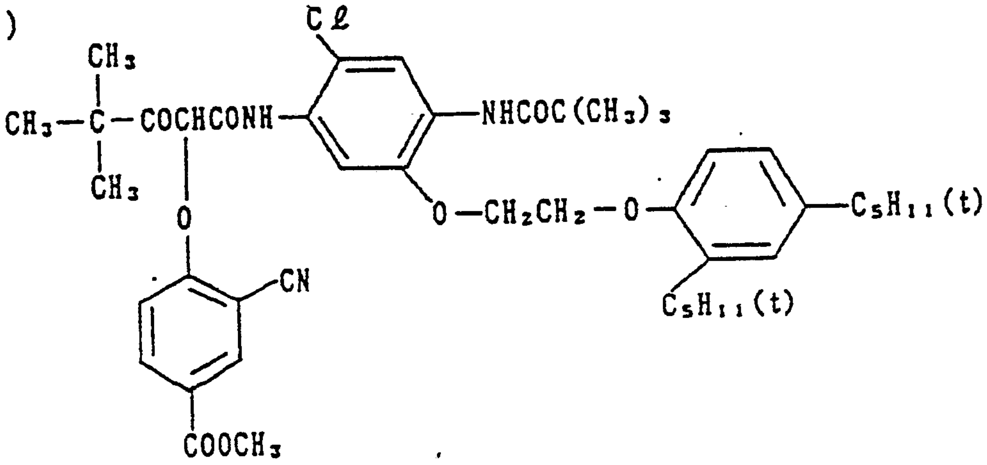
(Y－10)


OCH₃
CH₃
CH₃—C—COCHCONH—
CH₃
O
Cℓ
SO₂
Cℓ
OH
NHCOCHO—
C₂H₅
C₅H₁₁(t)
—C₅H₁₁(t)

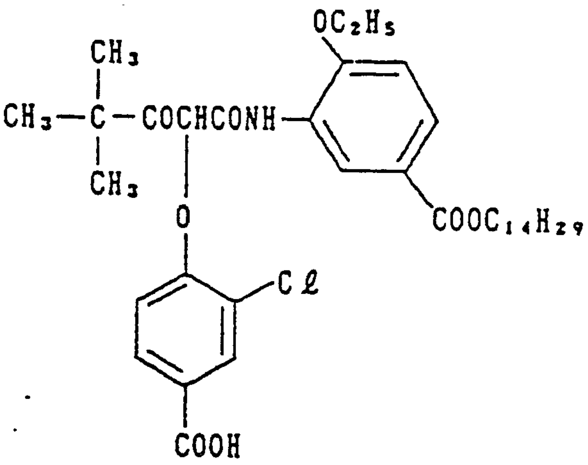
(Y-11)


OCH3
CH3
CH3—C—COCHCONH
CH3
O
SO2N
CH3
C18H37(n)
NH
SO2
CH3

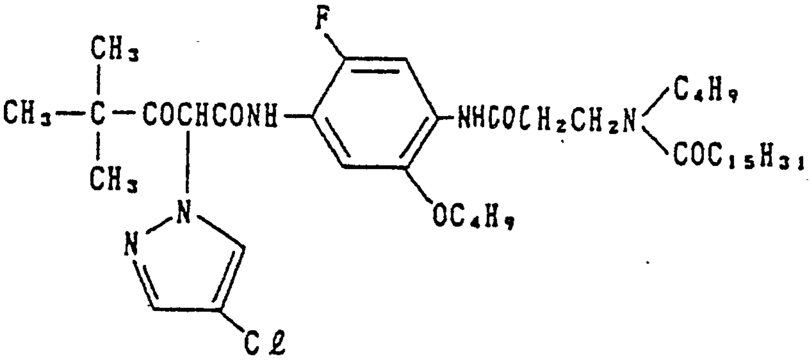
(Y-12)


Cℓ
CH3
CH3—C—COCHCONH
CH3
NHCOC(CH3)3
O
O—CH2CH2—O
C5H11(t)
C5H11(t)
CN
COOCH3

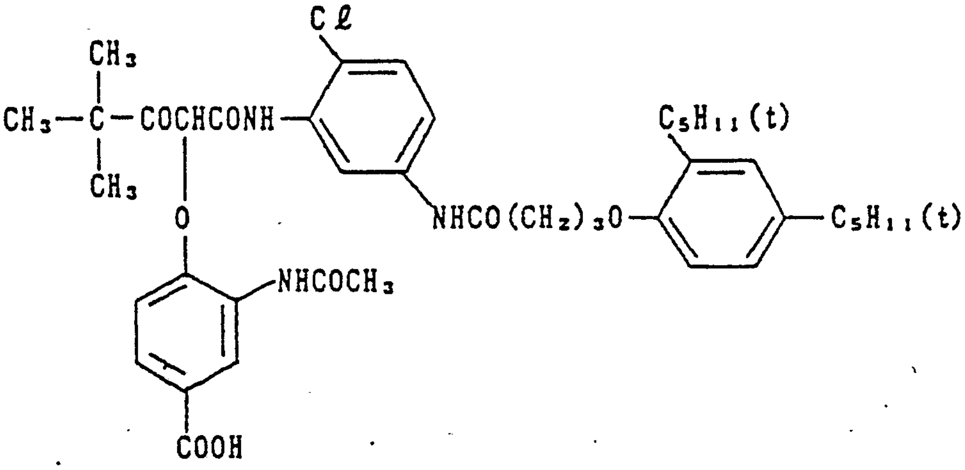
(Y－13)



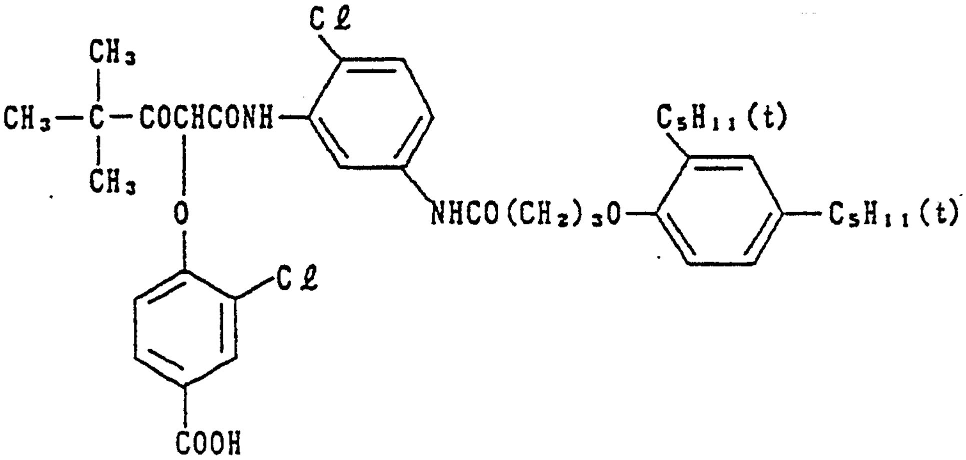
(Y－14)



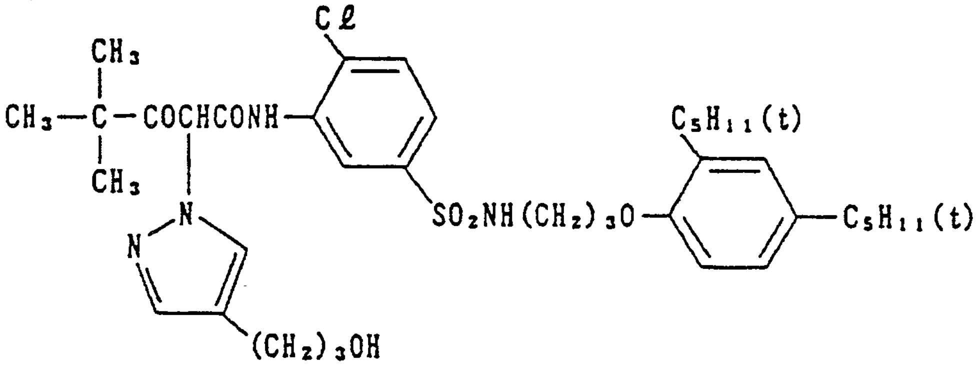
(Y－１５)


CH3
CH3—C—COCHCONH—
CH3
O
Cℓ
NHCOCH3
COOH
NHCO(CH2)3O—
C5H11(t)
—C5H11(t)

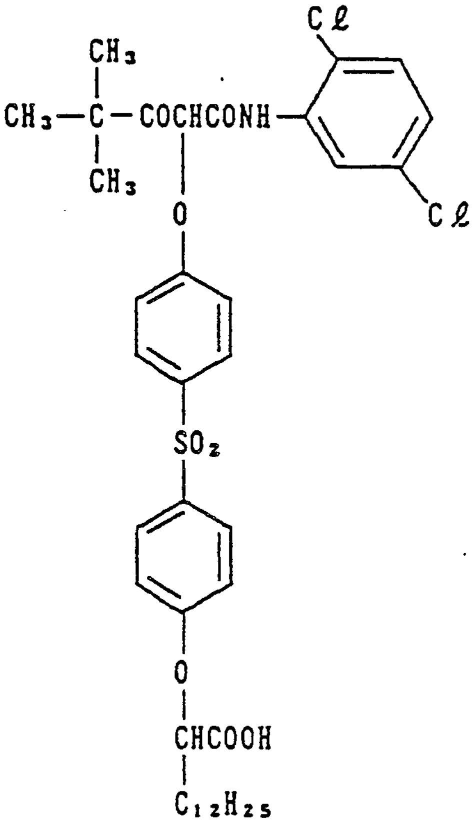
(Y－１６)


CH3
CH3—C—COCHCONH—
CH3
O
Cℓ
Cℓ
COOH
NHCO(CH2)3O—
C5H11(t)
—C5H11(t)

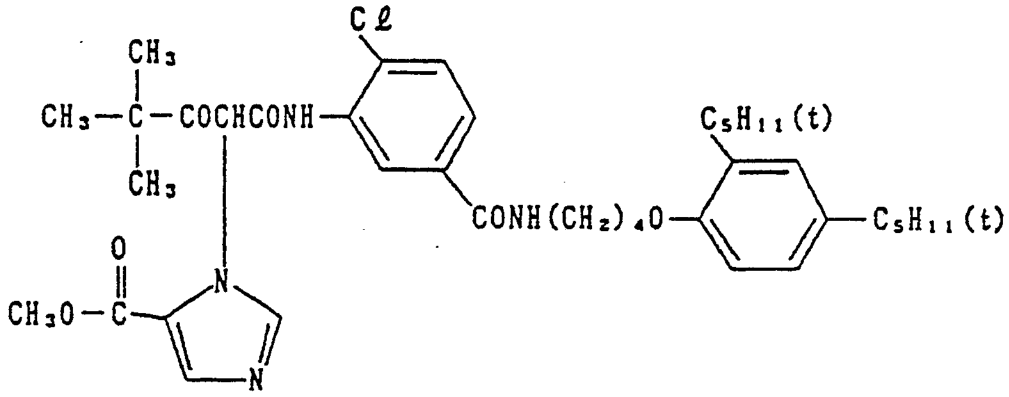
(Y－17)


Cℓ
CH₃
CH₃—C—COCHCONH—
CH₃
N
N
(CH₂)₃OH
SO₂NH(CH₂)₃O—
C₅H₁₁(t)
—C₅H₁₁(t)

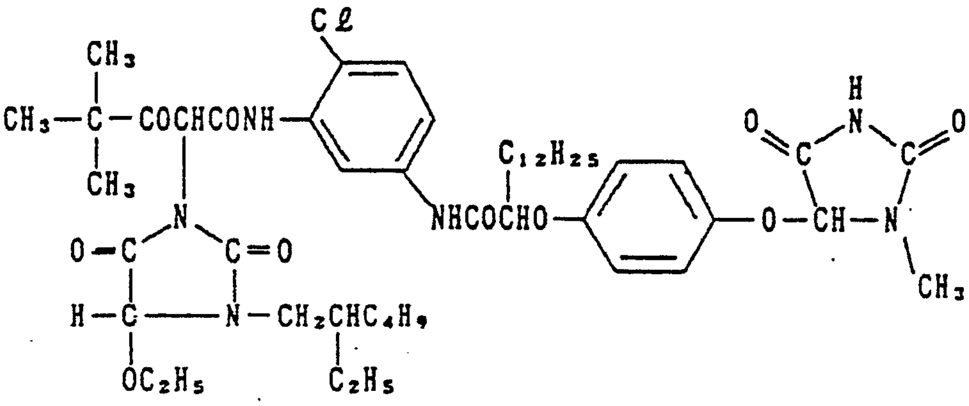
(Y－18)


Cℓ
CH₃
CH₃—C—COCHCONH—
CH₃
O
Cℓ
SO₂
O
CHCOOH
C₁₂H₂₅

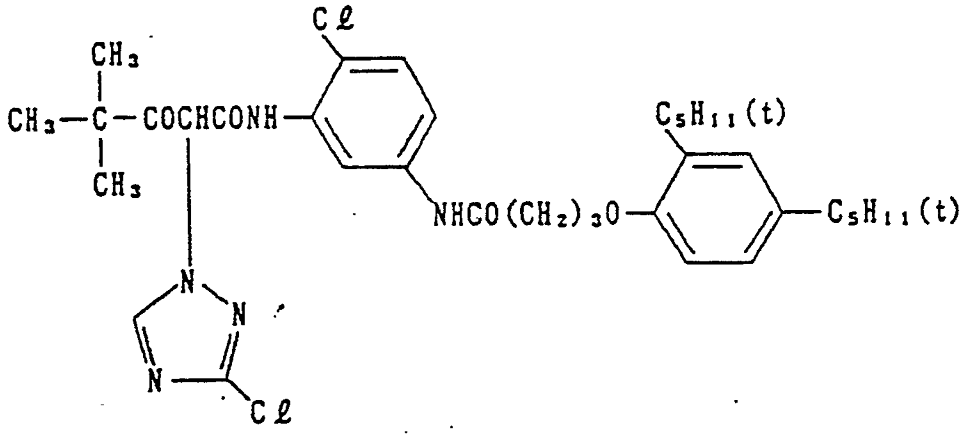
(Y－１９)



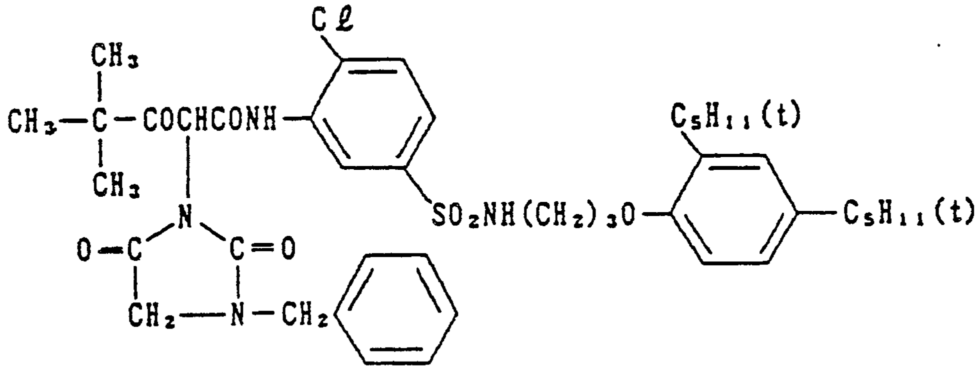
(Y－２０)



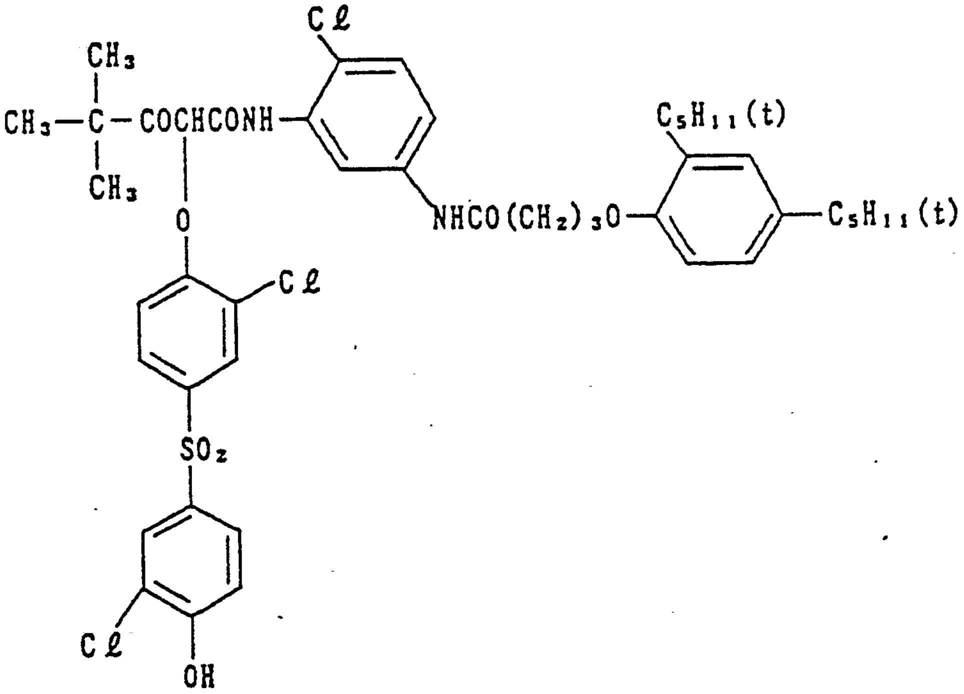
(Y-21)



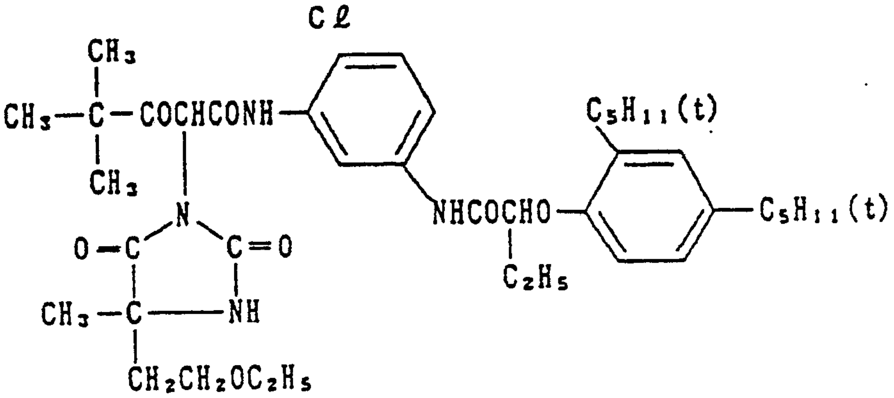
(Y-22)



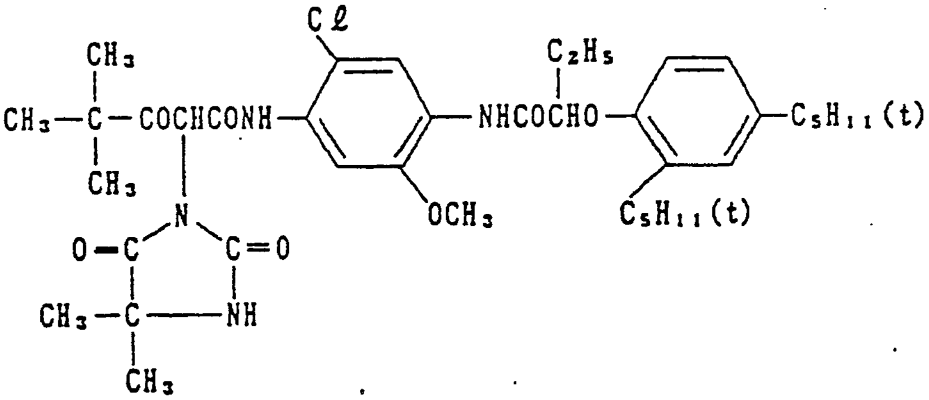
(Y－23)



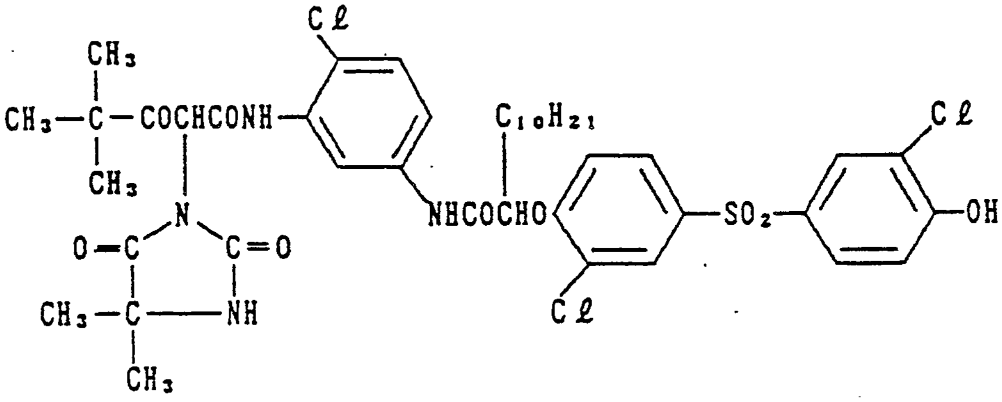
(Y－24)



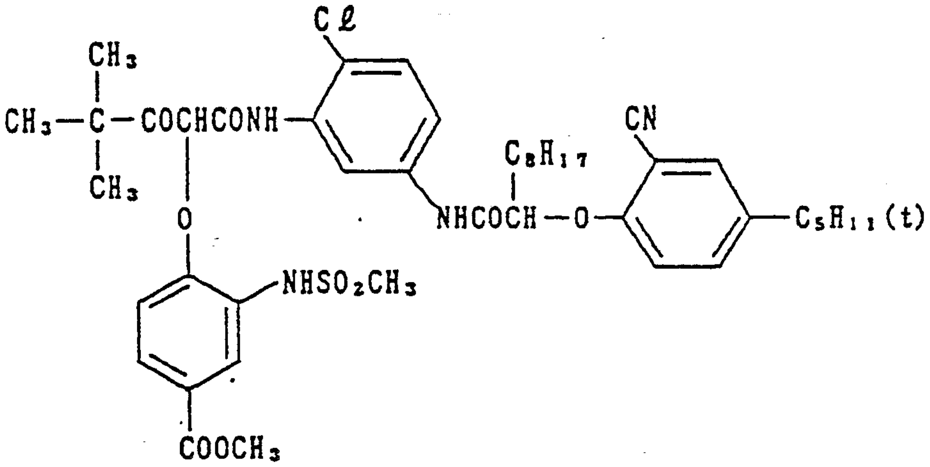
(Y－25)



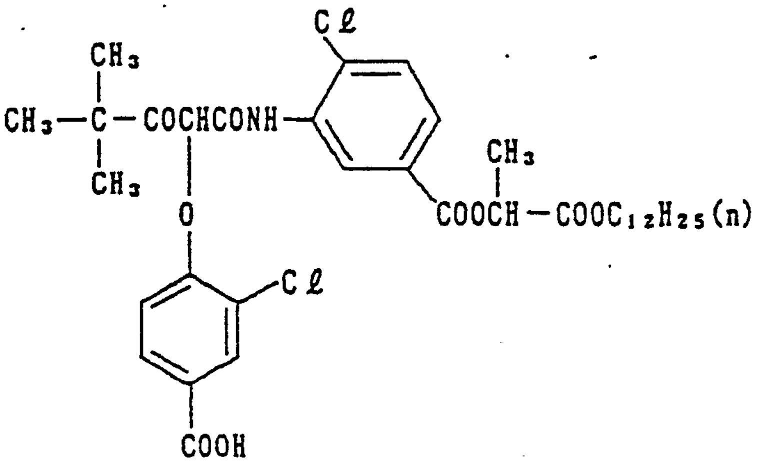
(Y－26)



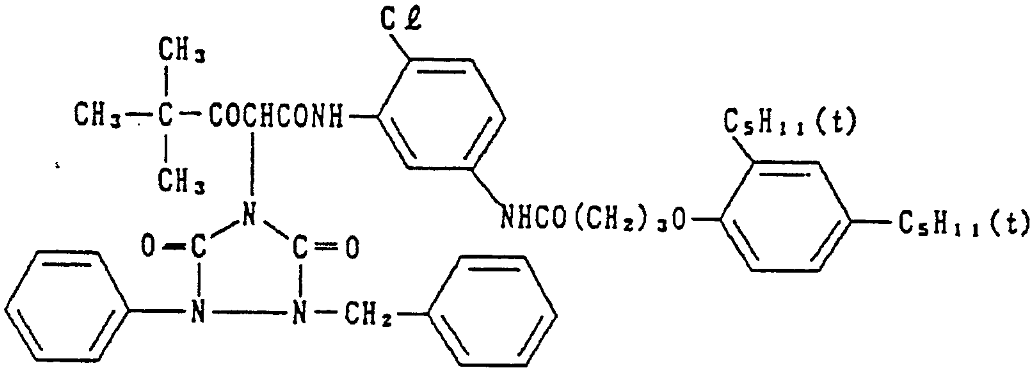
(Y－27)



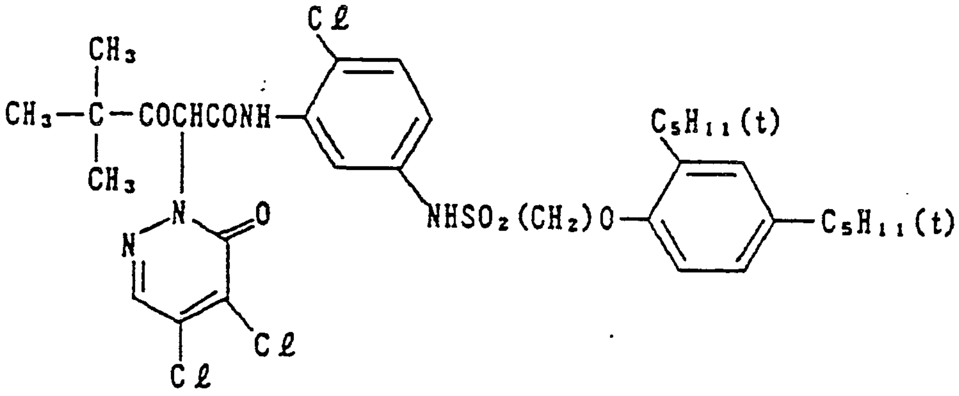
(Y－28)



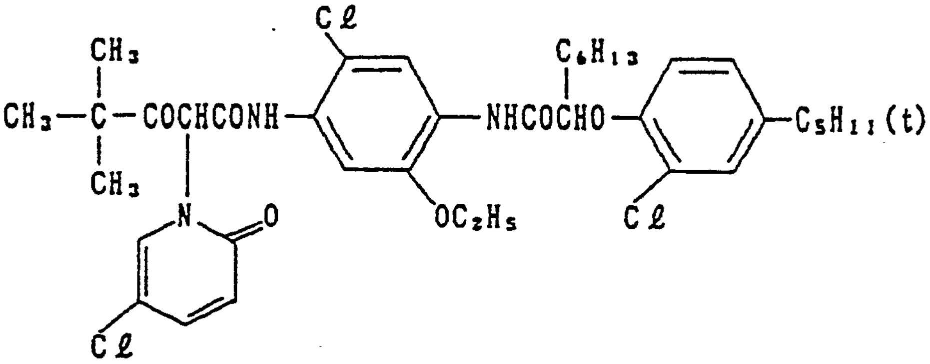
(Y－29)



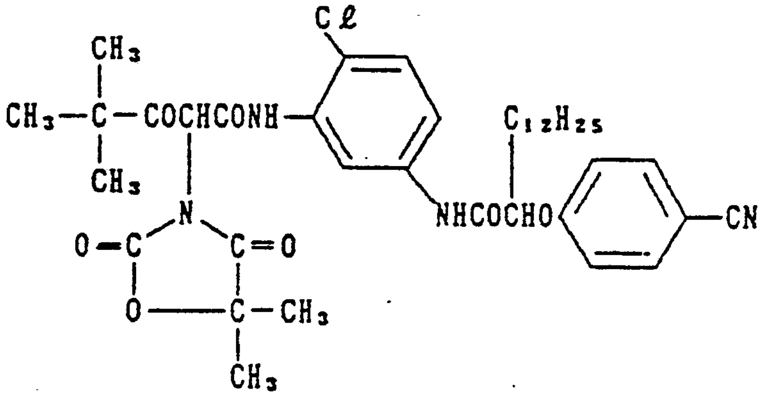
(Y－30)



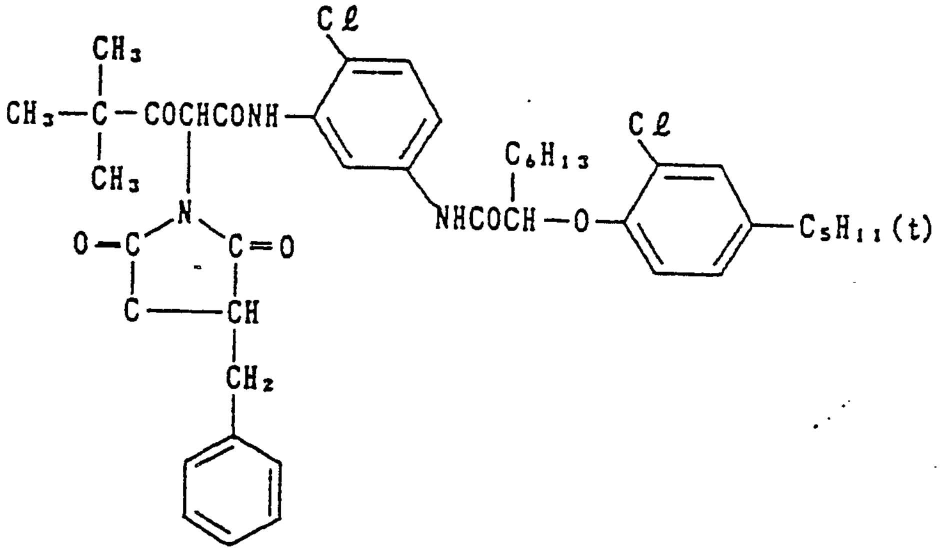
(Y－31)



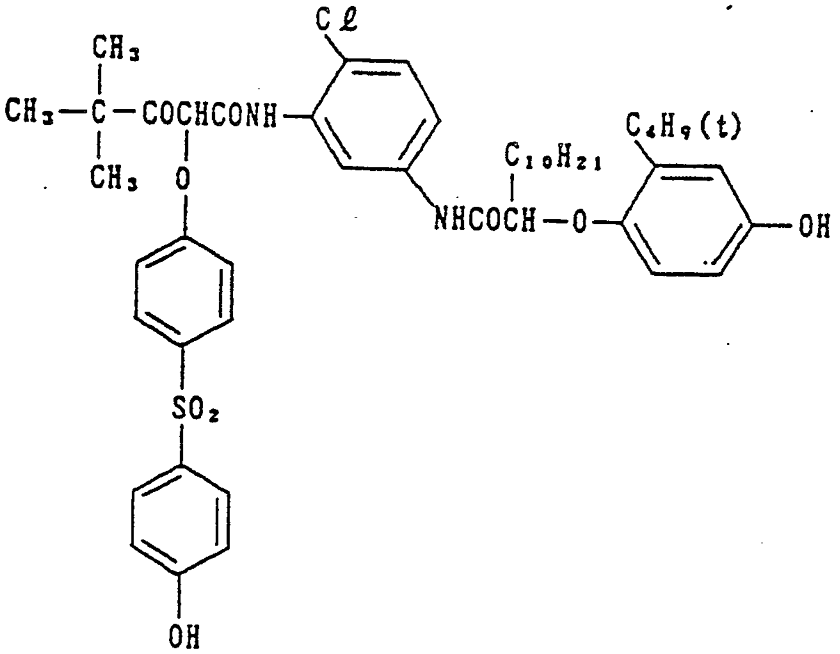
(Y－32)



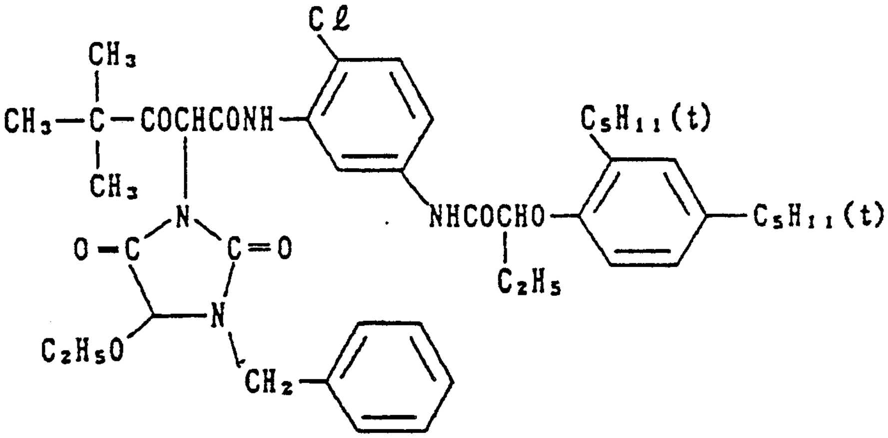
(Y－33)



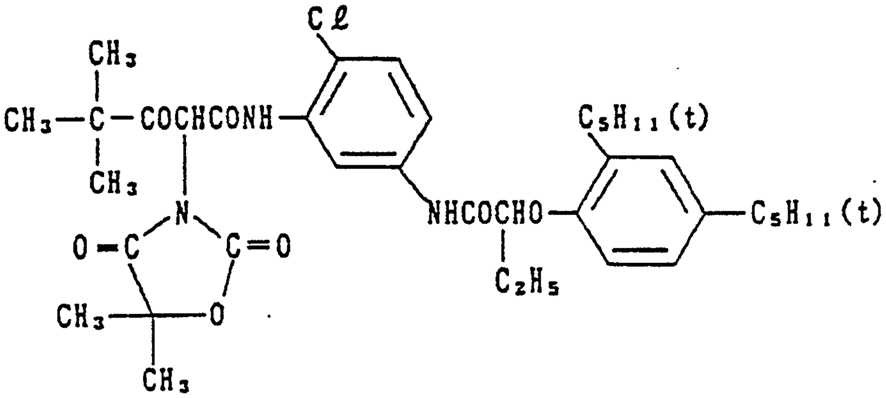
(Y－34)



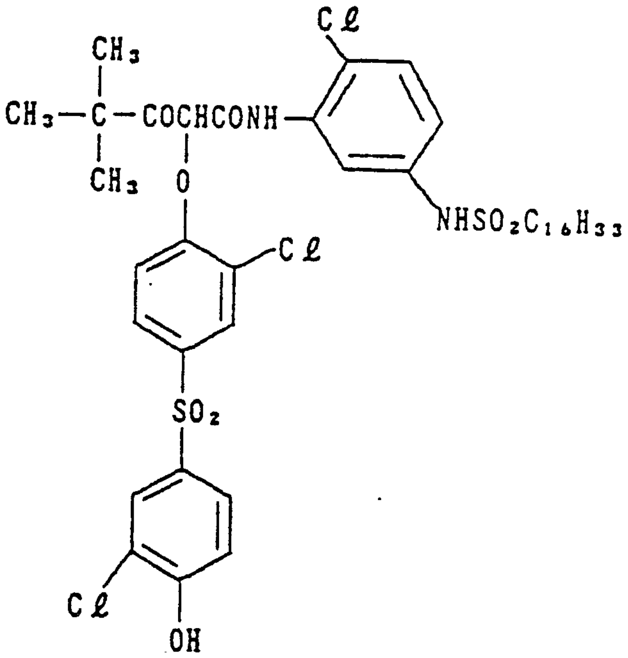
(Y－35)



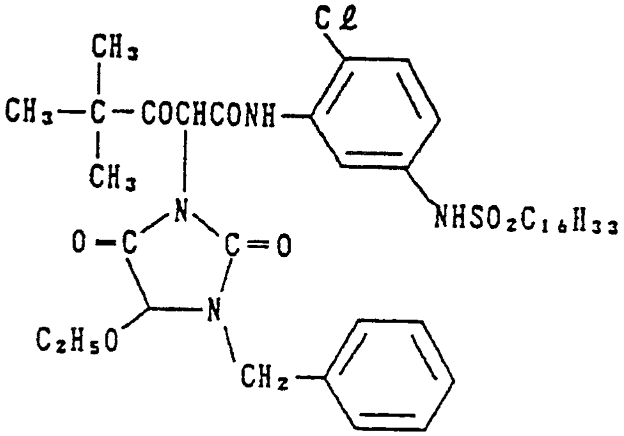
(Y－36)



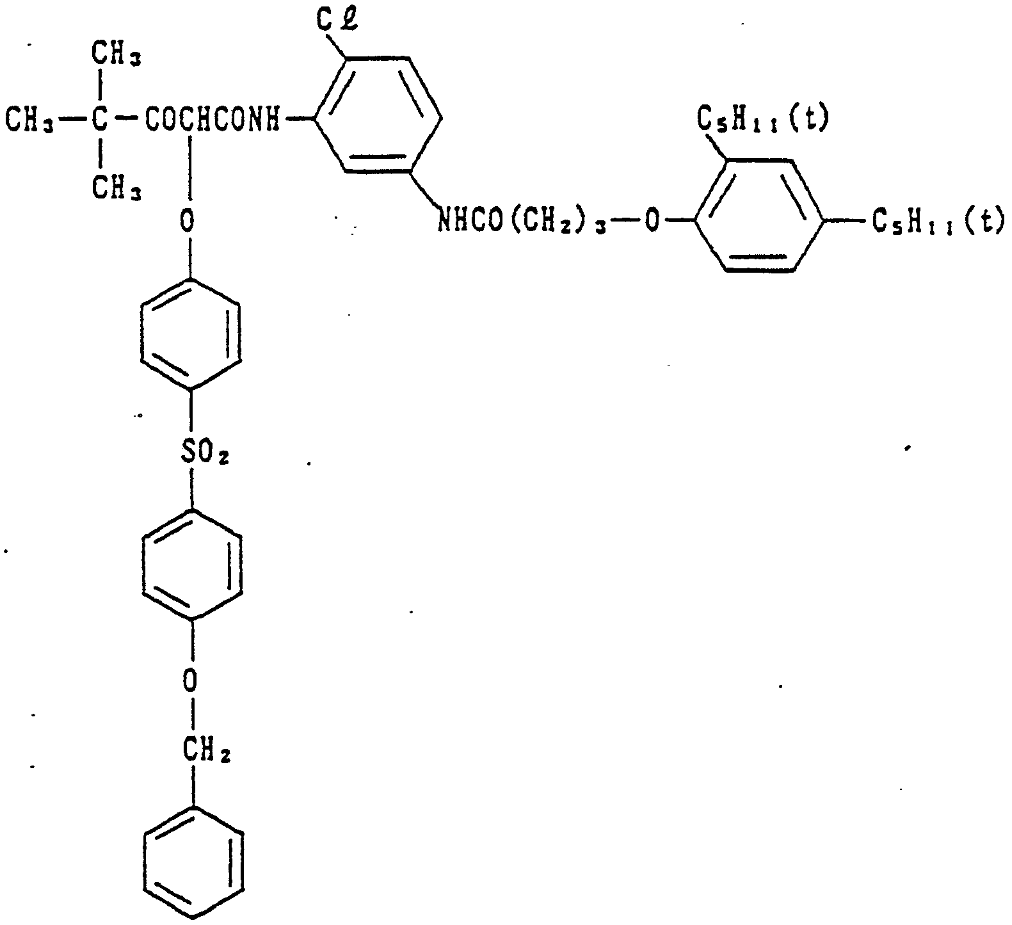
(Y－３７)


Cℓ
CH₃
CH₃—C—COCHCONH—
CH₃
O
NHSO₂C₁₆H₃₃
Cℓ
SO₂
Cℓ
OH

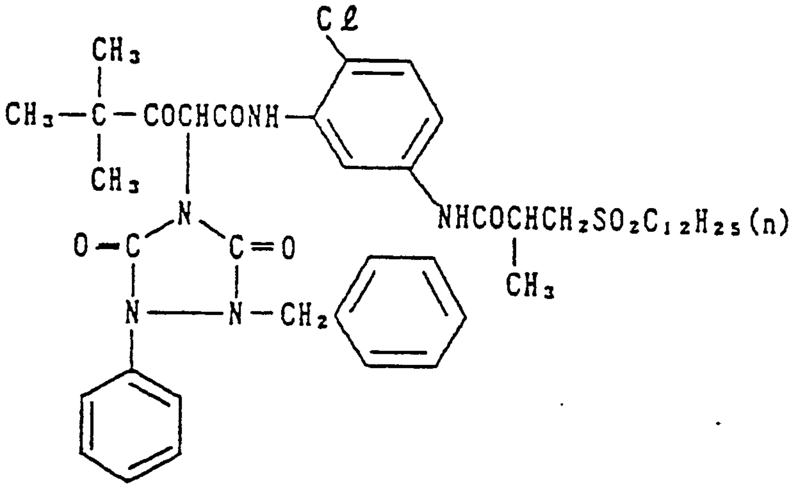
(Y－３８)


Cℓ
CH₃
CH₃—C—COCHCONH—
CH₃
NHSO₂C₁₆H₃₃
N
O=C
C=O
N
C₂H₅O
CH₂

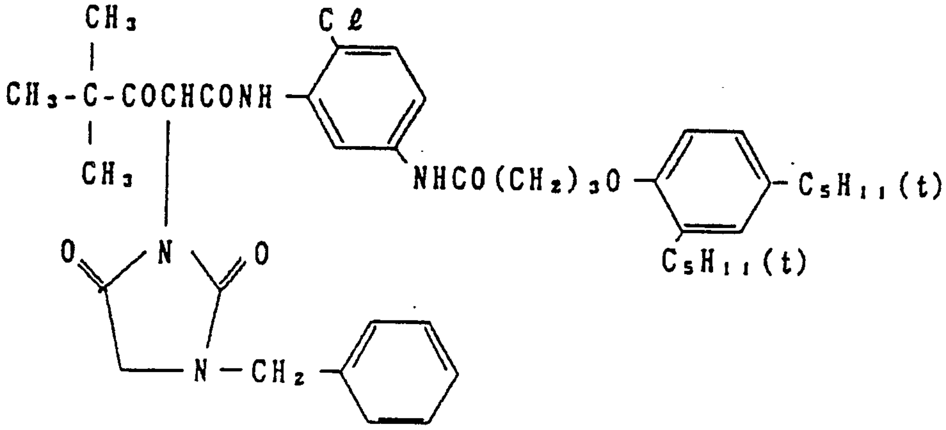
(Y－39)



(Y-40)



(Y-41)



Couplers having the formula (VI) are disclosed in JP-A-54-48541, JP-B-58-10739, U.S. Patent 4,326,024 and Research Disclosure, 18053, Vol. 180 (April, 1979).

The couplers having the formula (VI) are used in an amount of 0.1 to 1.1 mol, preferably 0.1 to 0.5 mol per mol of silver halide in the blue-sensitive silver halide emulsion.

Cyan couplers having the formula (VII) are illustrated in greater detail below.

In the formula (VII), suitable alkyl groups represented by R^{131} are a straight chain, branched or cyclic alkyl group having from 1 to 32 carbon atoms and suitable aryl groups are an aryl group having from 6 to 42 carbon atoms. When R^{131} is an amino group, the group R^{131} can be an alkylamino group or an arylamino group with a substituted or unsubstituted phenylamino group being preferred. The alkyl group, the aryl group or the phenylamino group represented by R^{131} may be substituted by one or more substituent groups selected from the group consisting of an alkyl group, an aryl group, an alkyl, or aryloxy group, a carboxyl group, an alkyl- or arylcarbonyl group, an alkyl- or aryloxycarbonyl group, an acyloxy group, a sulfamoyl group, a carbamoyl group, a sulfonamido group, an acylamino group, an imido group, a sulfonyl group, a hydroxy group, a cyano group and halogen. R^{133} and R^{132} may combine together to form a 5-membered to 7-membered ring. Preferred examples of such rings include an oxyindole ring, a 2-oxobenzimidazoline ring and a carbostyryl ring.

Z^{131} is a hydrogen atom or a group which is eliminated on coupling (a coupling eliminable group). Examples of groups which are eliminated on coupling include a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, a sulfonyloxy group, an amido group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an aliphatic or aromatic thio group, a heterocyclic thio group, an imido group, an N-substituted heterocyclic ring and an aromatic azo group. These groups may contain photographically useful groups.

A dimer or polymer may be formed by R^{131}, R^{132} or Z^{131} in the formula (VII).

Of the couplers having the formula (VII), couplers where R^{132} is an alkyl group having from 2 to 4 carbon atoms and couplers where R^{132} is a phenoxy-substituted alkanamido when R^{132} is an acylamino group are preferred. When R^{132} and R^{133} combine together to form a ring, 5-membered oxyindole ring couplers are preferred.

Cyan couplers having the formula (VIII) are illustrated in greater detail below.

Suitable alkyl groups represented by R^{134} are a straight chain, branched or cyclic alkyl group having from 1 to 32 carbon atoms, suitable aryl groups are an aryl group having from 6 to 42 carbon atoms and suitable heterocyclic groups are a 4-membered to 7-membered ring containing at least one of oxygen, nitrogen and sulfur atoms. These groups may be optionally substituted by substituent groups already described above for R^{131} in the formula (VII). Z^{131} is a hydrogen atom or a group which is eliminated on coupling and as defined above for Z^{131} in the formula (VII).

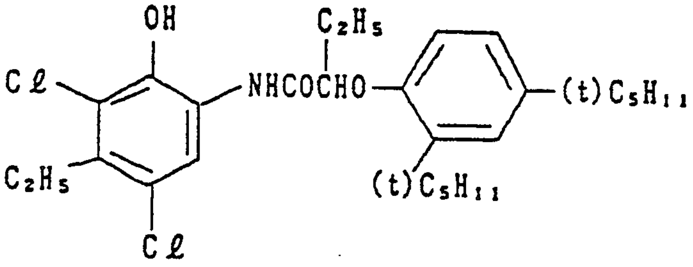
A dimer or polymer may be formed by R^{134}, R^{135}, R^{136} or Z^{131} in the formula (VIII).

Of the couplers having the formula (VIII), couplers where R^{136} is a hydrogen atom, p is 1, and R^{135} is an acyl group or an alkoxycarbonyl group are particularly preferred.

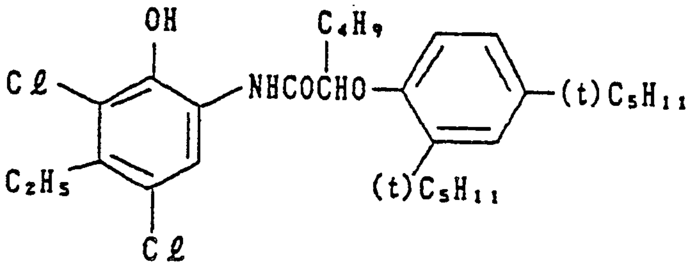
When the couplers having the formula (VII) are compared with the couplers having the formula (VIII), the couplers having the formula (VII) are preferable for the purpose of the present invention.

Examples of couplers having the formulae (VII) and (VIII) which can be used in the present invention include, but are not limited to, the following compounds.

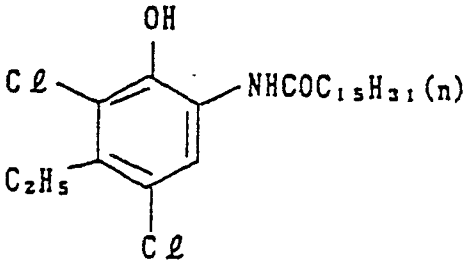
(C－1)


OH
C_2H_5
Cℓ
NHCOCHO
$(t)C_5H_{11}$
C_2H_5
$(t)C_5H_{11}$
Cℓ

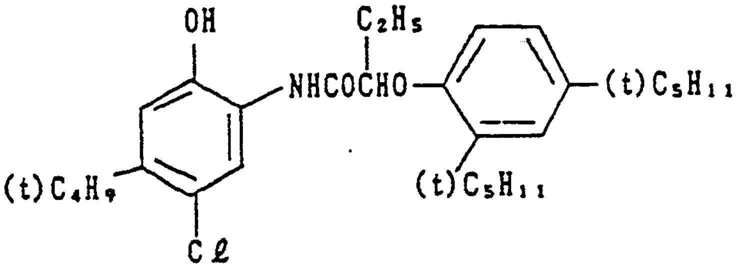
(C－2)


OH
C_4H_9
Cℓ
NHCOCHO
$(t)C_5H_{11}$
C_2H_5
$(t)C_5H_{11}$
Cℓ

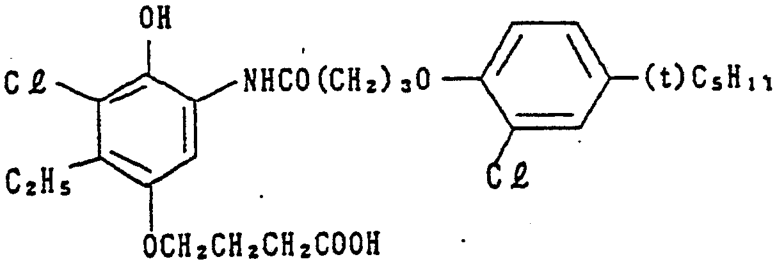
(C－3)


OH
Cℓ
$NHCOC_{15}H_{31}(n)$
C_2H_5
Cℓ

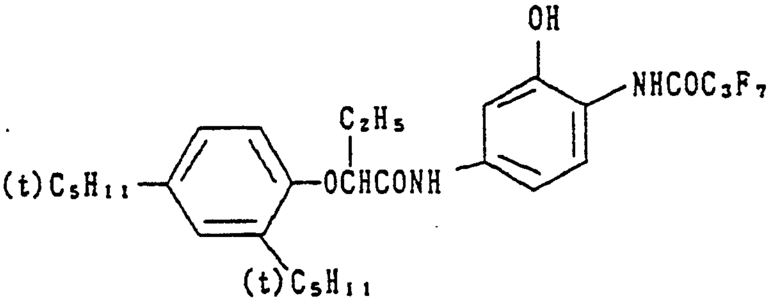
(C－4)


OH
C₂H₅
NHCOCHO
(t)C₅H₁₁
(t)C₄H₉
(t)C₅H₁₁
Cℓ

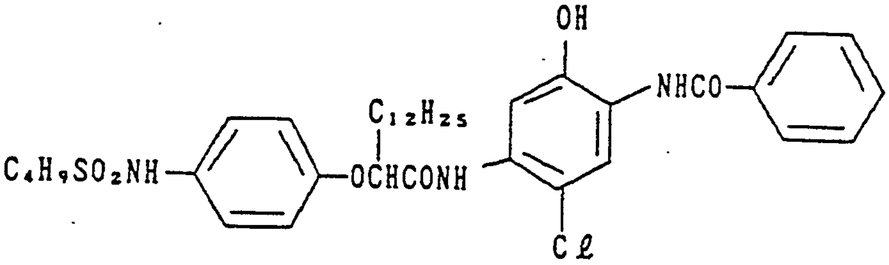
(C－5)


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

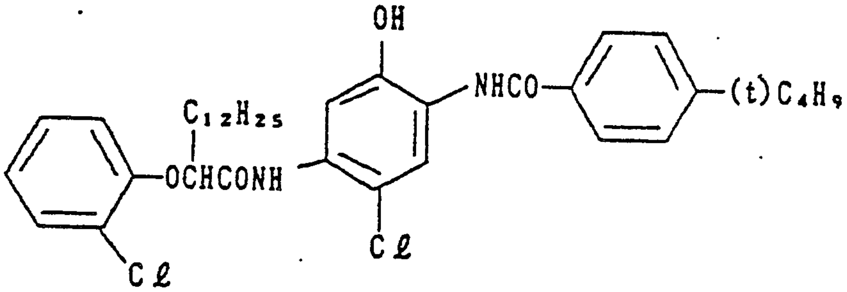
(C－6)


OH
NHCOC₃F₇
C₂H₅
(t)C₅H₁₁
OCHCONH
(t)C₅H₁₁

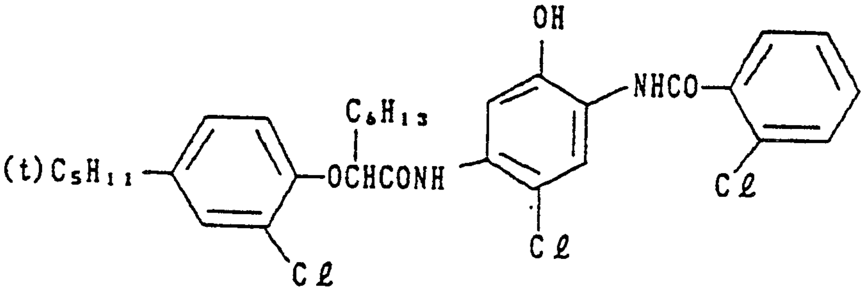
(C－7)


OH
NHCO
C₁₂H₂₅
C₄H₉SO₂NH
OCHCONH
Cℓ

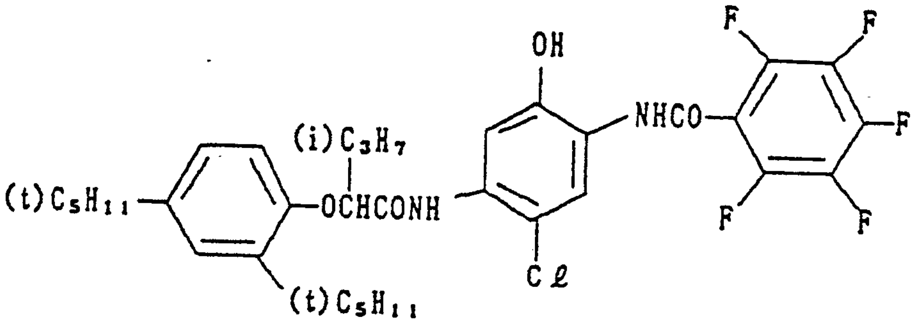
(C－8)


OH
NHCO
(t)C₄H₉
C₁₂H₂₅
OCHCONH
Cℓ
Cℓ

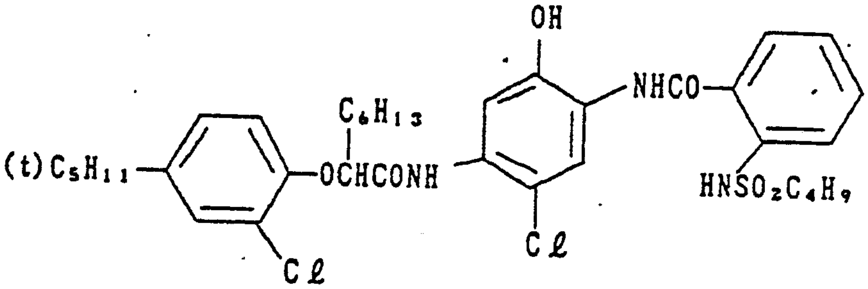
(C－9)


OH
NHCO
C₆H₁₃
(t)C₅H₁₁
OCHCONH
Cℓ
Cℓ
Cℓ

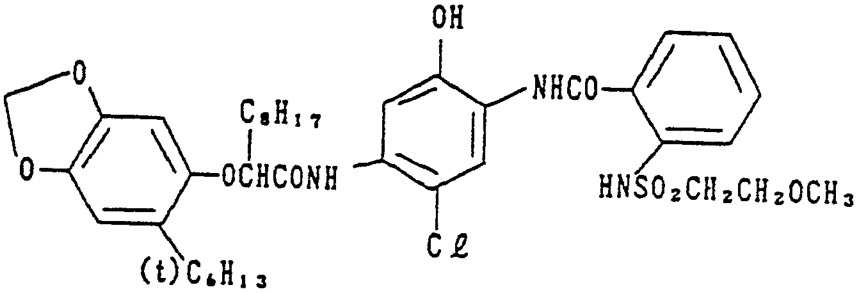
(C－１０)


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

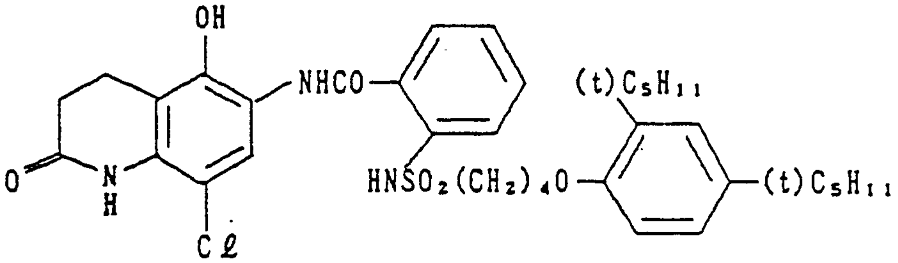
(C－１１)


OH
NHCO
C₆H₁₃
(t)C₅H₁₁
OCHCONH
HNSO₂C₄H₉
Cℓ
Cℓ

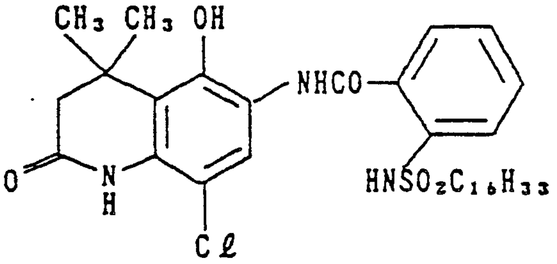
(C－１２)


OH
O
NHCO
C₈H₁₇
O
OCHCONH
HNSO₂CH₂CH₂OCH₃
Cℓ
(t)C₆H₁₃

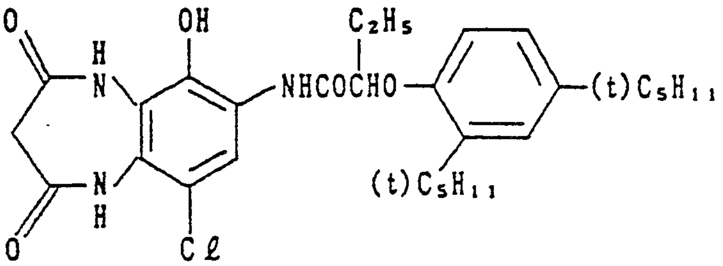
(C－13)



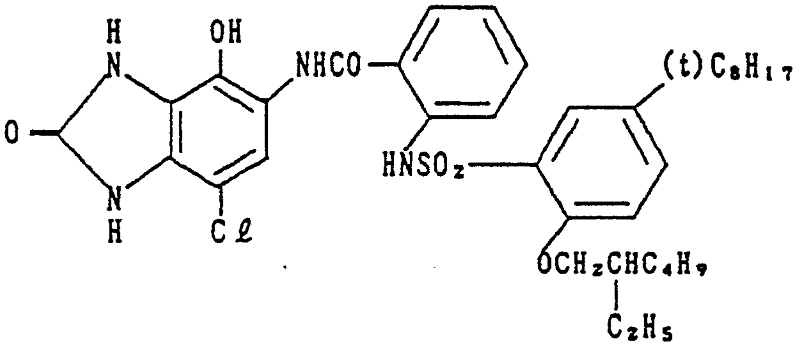
(C－14)



(C－15)

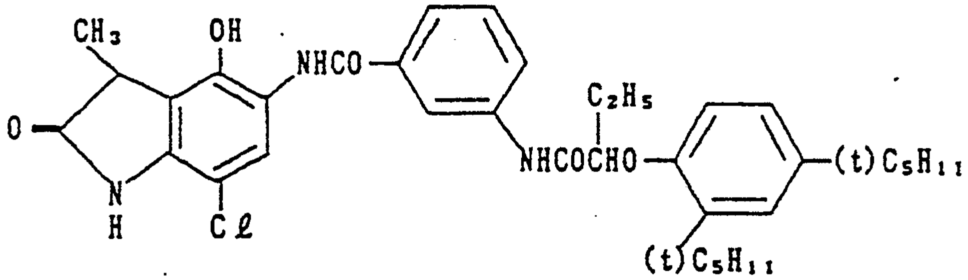


(C－16)



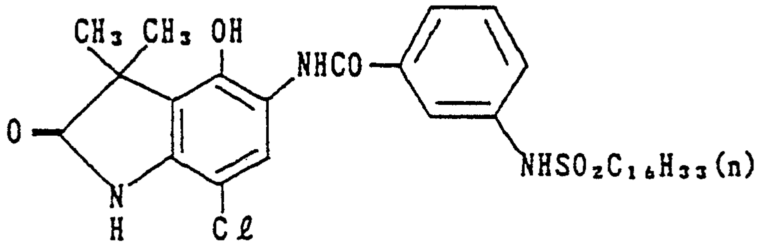
H
OH
NHCO
(t)C₈H₁₇
O
HNSO₂
N
H
Cℓ
OCH₂CHC₄H₉
C₂H₅

(C－17)



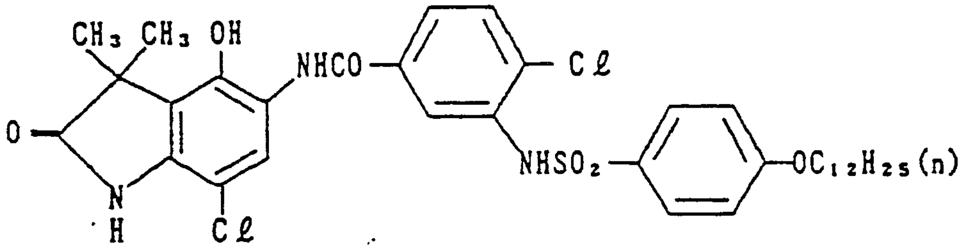
CH₃
OH
NHCO
C₂H₅
O
NHCOCHO
(t)C₅H₁₁
N
H
Cℓ
(t)C₅H₁₁

(C－18)

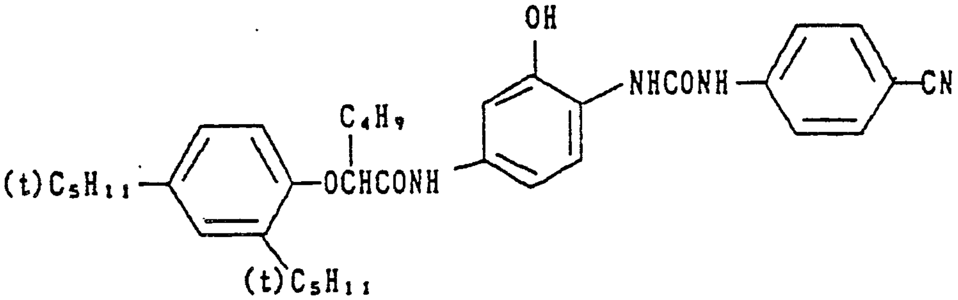


CH₃ CH₃ OH
NHCO
O
NHSO₂C₁₆H₃₃(n)
N
H
Cℓ

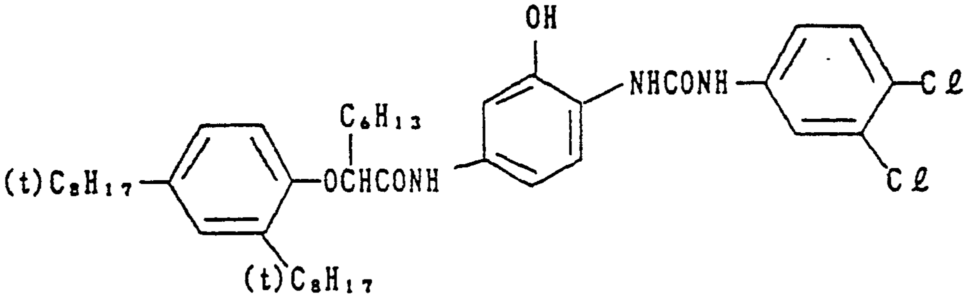
(C－19)



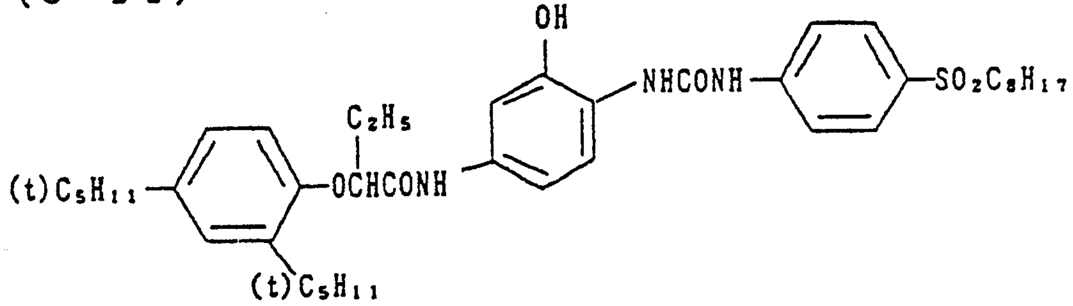
(C－20)



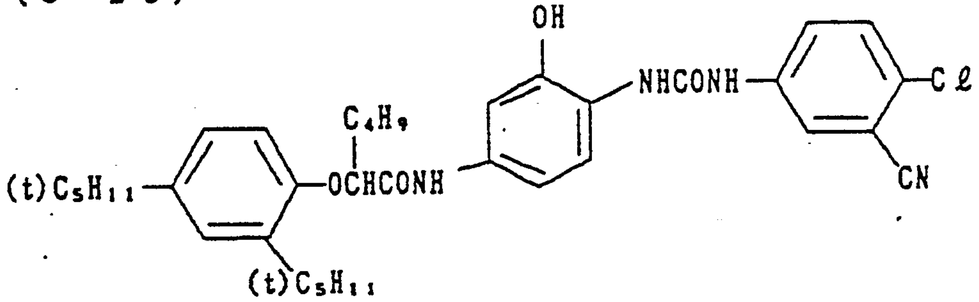
(C－21)



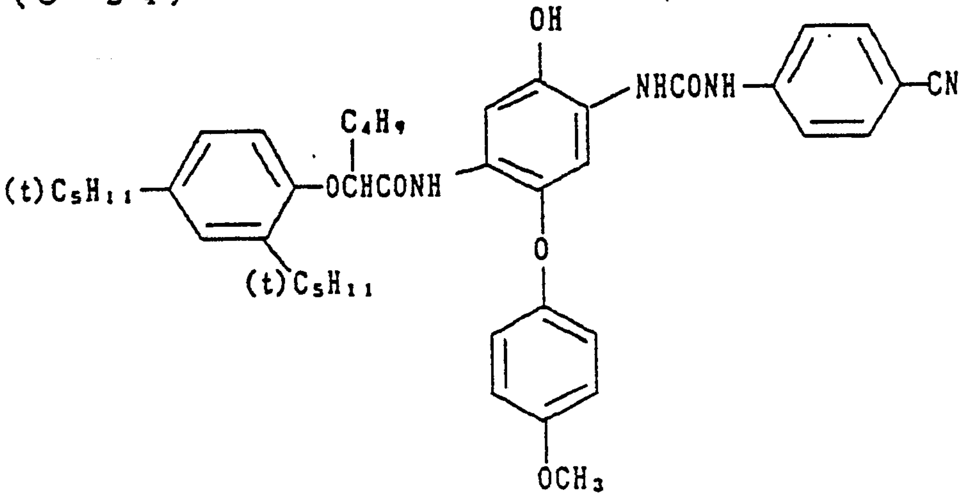
(C－22)


OH
NHCONH
SO₂C₈H₁₇
C₂H₅
(t)C₅H₁₁
OCHCONH
(t)C₅H₁₁

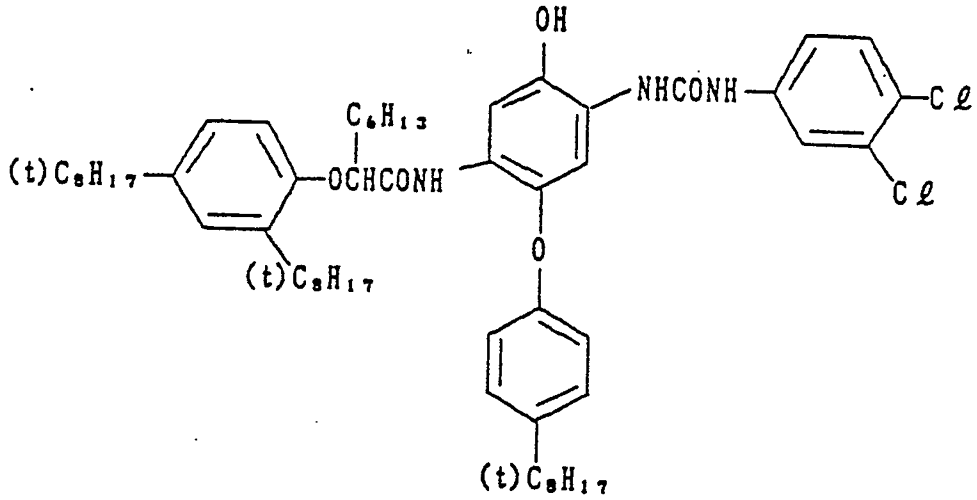
(C－23)


OH
NHCONH
Cℓ
C₄H₉
(t)C₅H₁₁
OCHCONH
CN
(t)C₅H₁₁

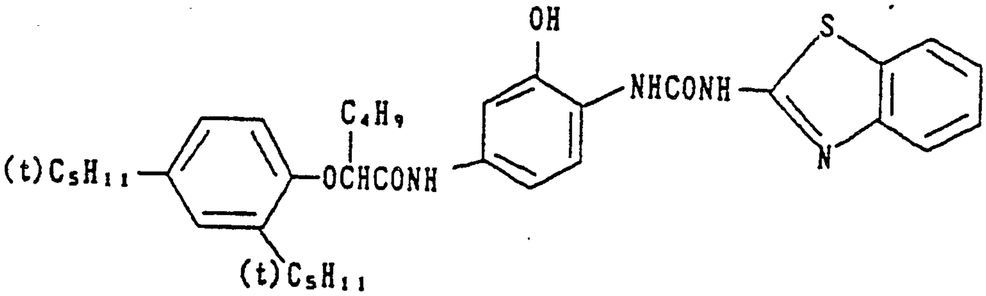
(C－24)


OH
NHCONH
CN
C₄H₉
(t)C₅H₁₁
OCHCONH
(t)C₅H₁₁
O
OCH₃

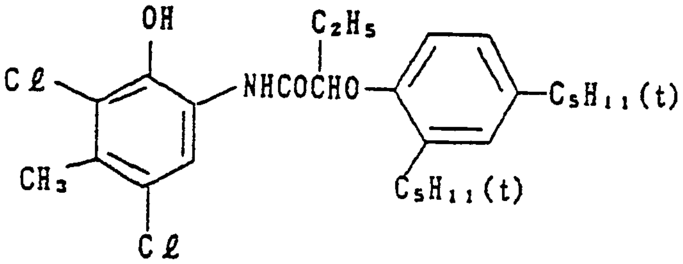
(C－25)


OH
NHCONH
Cℓ
Cℓ
C₆H₁₃
(t)C₈H₁₇
OCHCONH
(t)C₈H₁₇
O
(t)C₈H₁₇

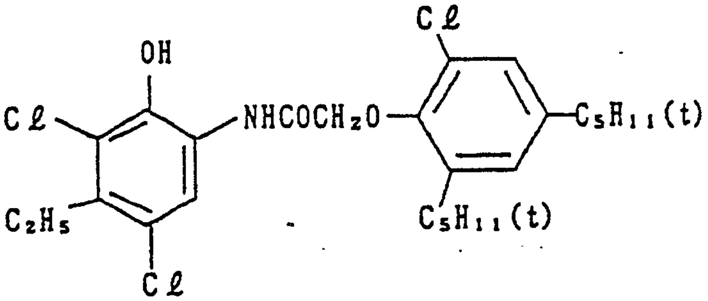
(C－26)


OH
NHCONH
S
N
C₄H₉
(t)C₅H₁₁
OCHCONH
(t)C₅H₁₁

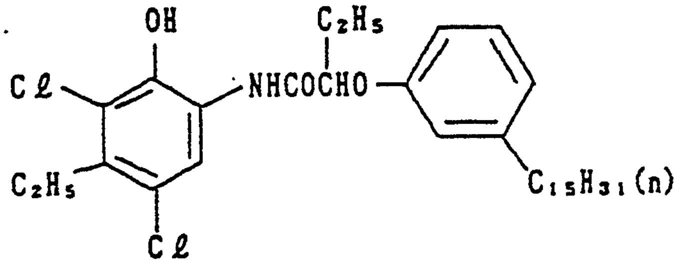
(C－27)


OH
C₂H₅
Cℓ
NHCOCHO
C₅H₁₁(t)
CH₃
C₅H₁₁(t)
Cℓ

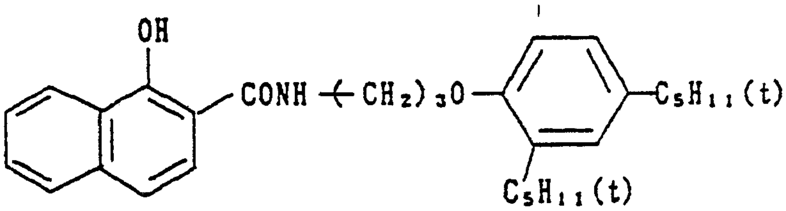
(C-28)


OH
Cℓ
Cℓ
C₂H₅
Cℓ
NHCOCH₂O
C₅H₁₁(t)
C₅H₁₁(t)

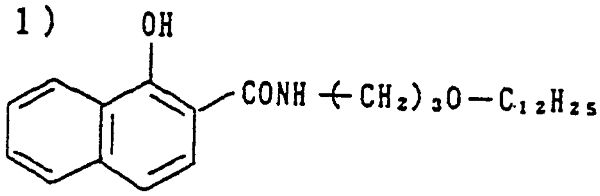
(C-29)


OH
Cℓ
C₂H₅
Cℓ
C₂H₅
NHCOCHO
C₁₅H₃₁(n)

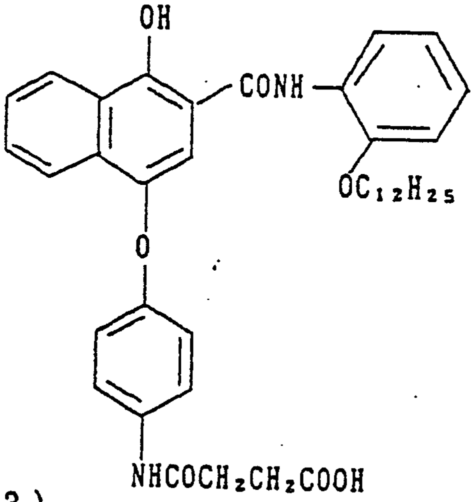
(C-30)


OH
CONH ⟮CH₂⟯₃O
C₅H₁₁(t)
C₅H₁₁(t)

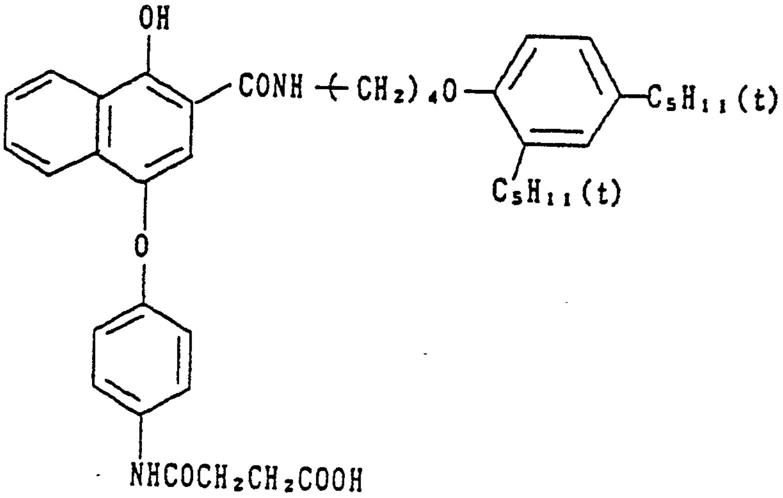
(C－31)


OH
CONH ⟵CH₂)₃O—C₁₂H₂₅

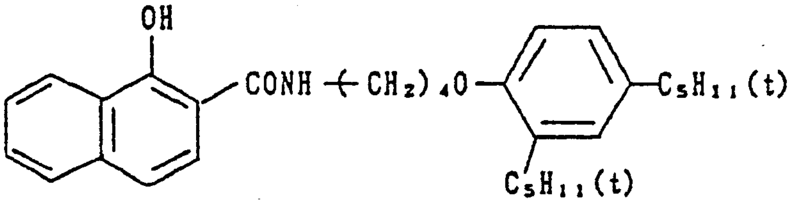
(C－32)


OH
CONH
OC₁₂H₂₅
O
NHCOCH₂CH₂COOH

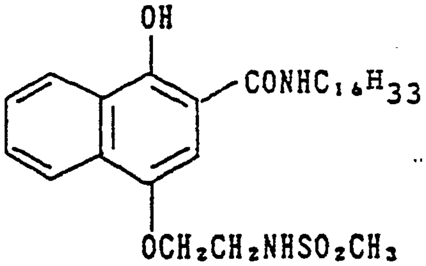
(C－33)


OH
CONH ⟵CH₂)₄O
C₅H₁₁(t)
C₅H₁₁(t)
O
NHCOCH₂CH₂COOH

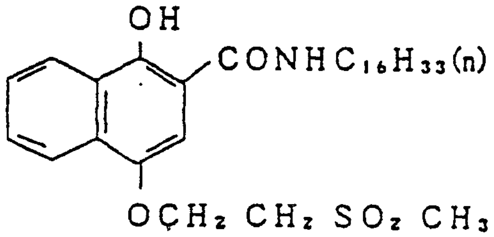
(C－34)


OH
CONH ⟵CH₂)₄O
C₅H₁₁(t)
C₅H₁₁(t)

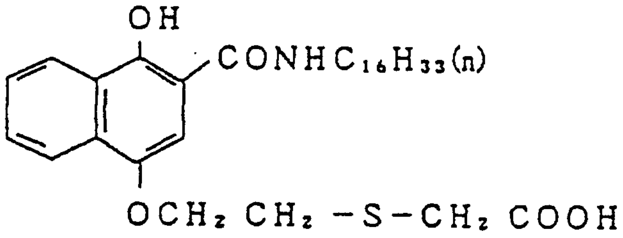
(C－35)


OH
CONHC₁₆H₃₃
OCH₂CH₂NHSO₂CH₃

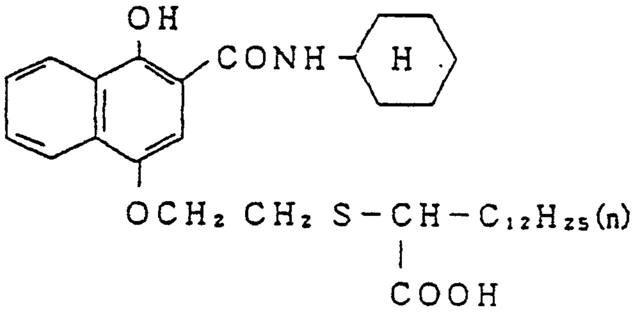
(C-36)



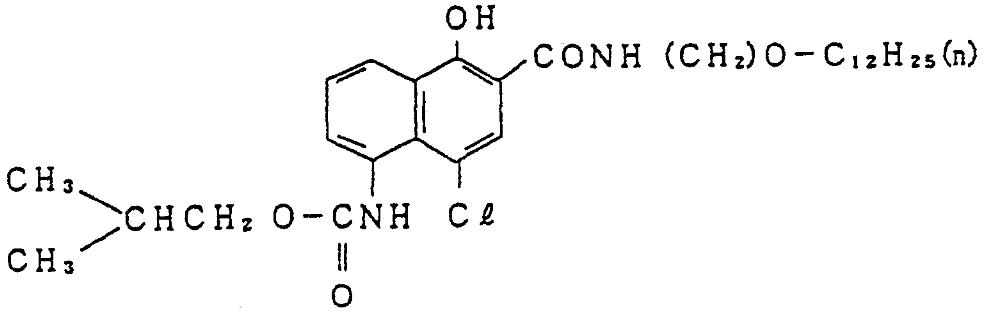
(C-37)



(C-38)



(C－39)



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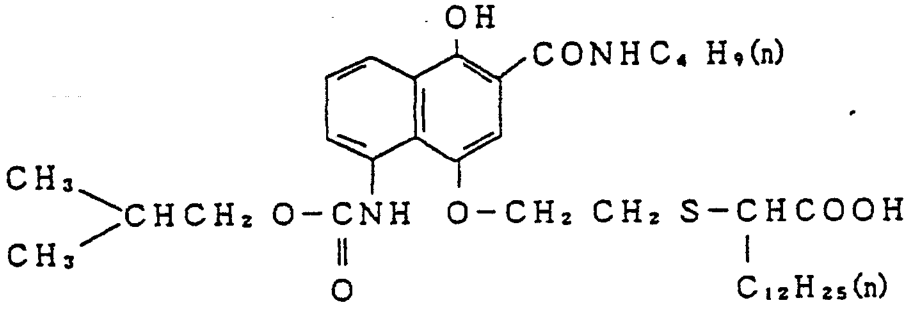

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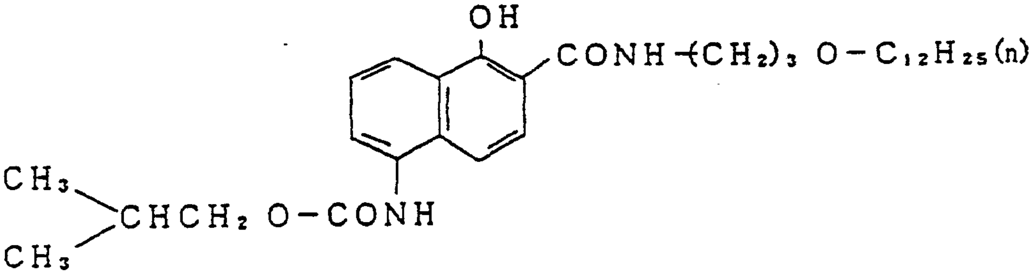

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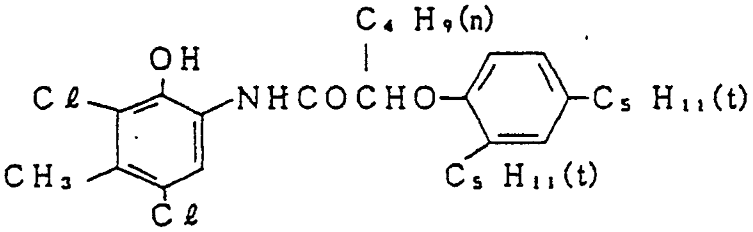

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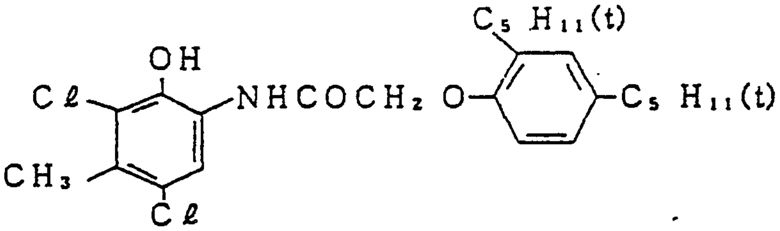

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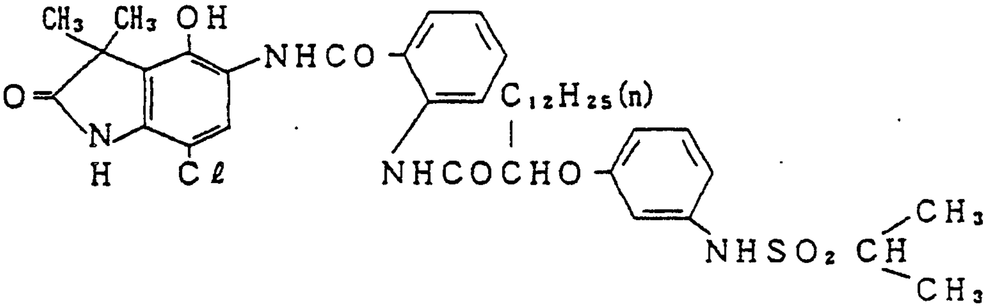

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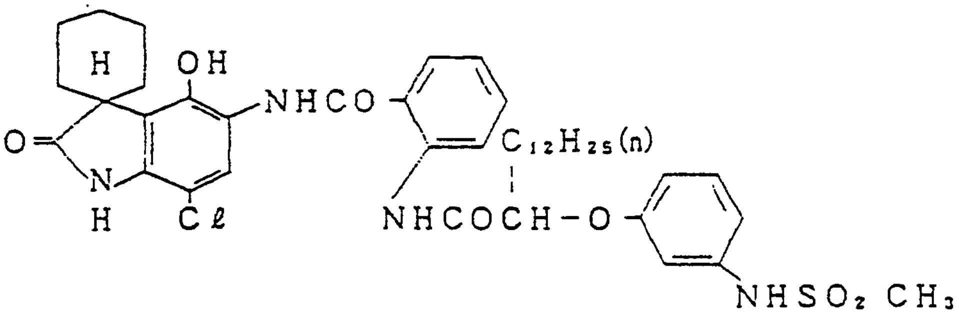

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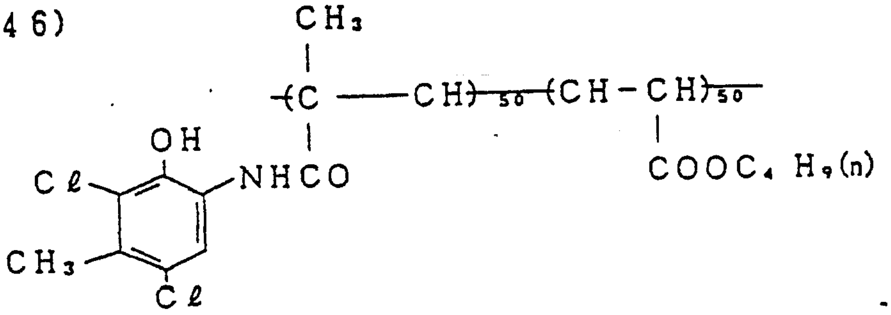
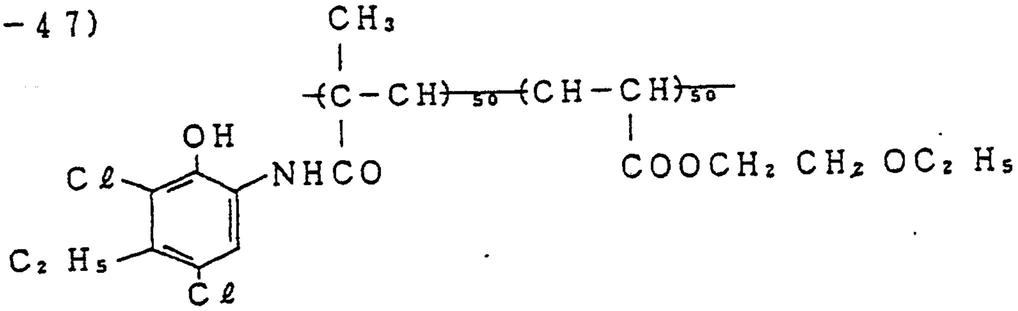
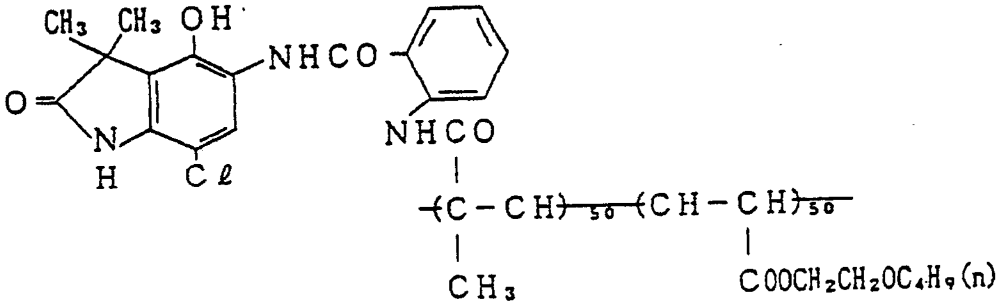


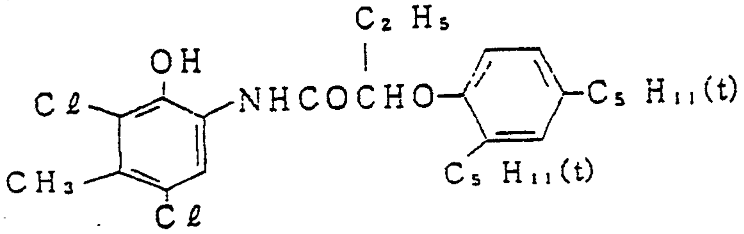
(C-47)



(C-48)



(C-49)



Couplers having the formula (VII) or (VIII) are described in U.S. Patents 2,801,171, 2,895,862 and 3,772,002, JP-A-59-124341, JP-A-58-105229, JP-A-60-24547, JP-A-60-237448, JP-A-61-39045 and JP-A-61-77245.

Though there is no particular limitation with regard to the amount of the cyan couplers having the formula (VII) or (VIII) to be used, these couplers are used in an amount of generally 0.01 to 2.0 mol, preferably 0.1 to 1.0 mol, per mol of silver halide.

Couplers having the formula (V), (VI), (VII) or (VIII) can be dispersed in hydrophilic colloids by dissolving them in high boiling organic solvents (e.g., phthalic esters, phosphoric acid esters, fatty acid esters, etc.).

Any of silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide and silver chloride can be used as the silver halide in the photographic emulsion layers of the photographic material of the present invention.

The silver halide grains of the present invention may be regular grains having a regular crystal form such as that of a cube, an octahedron or a tetradecahedron, irregular grains having an irregular crystal form such as that of a sphere, grains having crystalline defects such as a twin plane, or grains having a composite form thereof. A mixture of gains having various crystal forms may be used, if desired.

The silver halide grains may have such a wide grain size range of fine grains having a grain size of not greater than about 0.1 µm to large sized grains having a projected area diameter of about 10 µm. A monodisperse emulsion having a narrow grain size distribution or a polydisperse emulsion having a wide grain size distribution may be used.

Silver halide photographic emulsions which can be used in the present invention can be prepared by conventional methods, for example, the methods described in Research Disclosure, Vol. 176, No. 17643, pages 22 and 23 (December, 1978), "I. Emulsion Preparation and Types", and ibid., Vol. 187, No. 18716, page 648 (November, 1979).

The photographic emulsions of the present invention can be prepared according to the methods described in P. Glafkides, Chimie et Physique Photographique (Paul Montel, 1967), G.F. Duffin, Photographic Emulsion Chemistry (Focal Press, 1966) and V.L. Zelikman et al., Making and Coating Photographic Emulsion (Focal Press, 1964). Namely, any of an acid process, a neutral process and an ammonia process can be used. A soluble silver salt and a soluble halogen salt can be reacted in accordance with a single jet process, a double jet process or a combination thereof. A reverse mixing method in which grains are formed in the presence of excess silver ion can also be used. Further, a controlled double jet process in which the pAg in a liquid phase in which the silver halide is formed is maintained constant can be used. According to this method, a silver halide emulsion in which crystal form is regular and grain size is approximately uniform can be obtained.

Physical ripening can be carried out in the presence of conventional solvents for silver halide (for example, ammonia and potassium rhodanide or thioethers or thione compounds described in U.S. Patent 3,271,157, JP-A-51-12360, JP-A-53-82408, JP-A-53-144319, JP-A-54-100717 or JP-A-54-155828). Using this method, a silver halide emulsion in which the crystal form is regular and the grain size distribution is nearly uniform can also be obtained.

Silver halide emulsions comprising the above-described regular grains can be obtained by controlling the pAg and the pH during the formation of the grains. These methods are described in, for example, Photographic Science and Engineering, Vol. 6, pages 159 to 165 (1962), Journal of Photographic Science, Vol. 12, pages 242 to 251 (1964), U.S. Patent 3,665,394 and British Patent 1,413,748.

Typical examples of monodisperse emulsions which can be used in the present invention include emulsions comprising silver halide grains having a mean grain size of not smaller than about 0.05 µm wherein at least 95 wt% thereof comprises grains having a grain size within ±40% of the mean grain size. Further, emulsions comprising grains having a means grain size of 0.15 to 2 µm wherein at least 95 wt% of the grains or at least 95% of the number of the grains comprises grains having a grain size within means grain size ± 20% can be used. Methods of preparing such emulsions are described in U.S. Patents 3,574,628 and 3,655,394 and British Patent 1,413,748. Monodisperse emulsions as described in JP-A-48-8600, JP-A-51-39027, JP-A-51-83097, JP-A-53-137133, JP-A-54-48521, JP-A-54-99419, JP-A-58-37635 and JP-A-58-49938 are preferably used.

Further, tabular (plate-form) grains having an aspect ratio of 5 or more can be used in the present invention. These tabular grains can be easily prepared by methods described in Gutoff, Photographic Science and Engineering, Vol. 14, pages 248 to 257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520 and British Patent 2,112,157. U.S. Patent 4,434,226 discloses that when tabular grains are used, there are the advantages that covering power is increased and the color sensitizing efficiency of sensitizing dyes is improved.

Grains whose crystals form is controlled using sensitizing dyes or certain additives during the formation of grains also can be used.

The crystal structure may be uniform or a different halogen composition may exist between the interior of grain and the surface thereof. The crystal structure may be a laminar structure. These grains are disclosed in British Patent 1,027,146, U.S. Patents 3,505,068 and 4,444,877 and JP-A-60-143331. Silver halide grains having different halogen compositions may be joined together by epitaxial bonding. Silver halide grains may be joined to compounds other than silver halide such as silver rhodanide and lead oxide. These grains are described in U.S. Patents 4,094,684, 4,142,900 and 4,459,353, British Patent 2,038,792, U.S. Patents 4,349,622, 4,395,478, 4,433,501, 4,463,087, 3,656,962 and 3,852,067 and JP-A-59-162540.

Grains having an internal latent image type grain structure formed by forming sensitivity specks (e.g., Ag_2S, Agn, Au, etc.) on the surface of crystal by chemical ripening and then growing silver halide around the specks can be used.

Cadmium salts, zinc salts, lead salts, thallium salts, iridium salts or complex salts thereof, rhodium salts or complex salts thereof, iron salts or complex salts thereof may be present during the formation of the silver halide grains or during physical ripening.

The emulsions of the present invention may be a surface latent image type emulsion wherein a latent image is mainly formed on the surfaces of the grains, or an internal latent image type emulsion wherein a latent image is mainly formed in the interior of the grains.

Further, direct reversal emulsions may be used. The direct reversal emulsions may be any of a solarization type, an internal latent image type, a light fogging type and a type using a nucleating agent. A combination of these types of emulsions can also be used.

Of these, it is preferred that an internal latent image type emulsion which was previously not fogged be used and fogged by light before or during processing or by using a nucleating agent to obtain a direct positive image.

Internal latent image type silver halide emulsions previously not fogged which can be used in the present invention are emulsions in which the surfaces of silver halide grains are previously not fogged and which comprise silver halide grains in which a latent image is predominantly formed in the interior of the grains. More specifically, these emulsions have the following properties. A transparent support is coated with a given amount of the silver halide emulsion and the coated support is exposed for a fixed period of 0.01 to 10 seconds to prepare a sample. The emulsion has properties such that the maximum density obtained by developing the sample in the following Developing Solution A (internal developing solution) at 20°C for 60 minutes and measuring the maximum density by a conventional photographic density measuring method is preferably at least 5 times, more preferably 10 times, the maximum density obtained by developing the sample in the following Developing Solution B (surface developing solution) at 18°C for 5 minutes and measuring the maximum density.

Internal Developing Solution A:	
Metol	2 g
Sodium Sulfite (anhydrous)	90 g
Hydroquinone	8 g
Sodium Carbonate (monohydrate)	52.5 g
KBr	5 g
KI	0.5 g
Water to make	1 liter

Surface Developing Solution B:	
Metol	2.5 g
L-Ascorbic Acid	10 g
$NaBO_2.4H_2O$	35 g
KBr	1 g
Water to make	1 liter

Examples of internal latent image type emulsions include conversion type silver halide emulsions as described in British Patent 1,011,062 and U.S. Patents 2,592,250 and 2,456,942 and core/shell type silver halide emulsions. Examples of core/shell type silver halide emulsions include emulsions as described in JP-A-47-32813, JP-A-47-32814, JP-A-52-134721, JP-A-52-156614, JP-A-53-60222, JP-A-53-66218, JP-A-53-66727, JP-A-55-127549, JP-A-57-136641, JP-A-58-70221, JP-A-59-208540, JP-A-59-216136, JP-A-60-107641, JP-A-60-247237, JP-A-61-2148, JP-A-61-3137, JP-B-56-18939, JP-B-58-1412, JP-B-58-1415, JP-B-58-6935, JP-B-58-108528, JP-A-62-194248, U.S. Patents 3,206,313, 3,317,322, 3,761,266, 3,761,276, 3,850,637, 3,923,513, 4,035,185, 4,395,478, 4,504,570, European Patent 0017148 and Research Disclosure, No. 16345 (November, 1977).

Soluble silver salt can be removed from the emulsions before or after physical ripening by water washing with noodle, flocculation precipitation method or ultrafiltration.

The emulsions of the present invention are generally subjected to physical ripening, chemical ripening and spectral sensitization and then used. Additives for these stages are described in Research Disclosure, No. 17643 (December, 1978) and ibid., No. 18716 (November, 1979) and are shown in the following Table.

Other conventional photographic additives which can be used in the present invention are also described in these two Research Disclosure (Rd) references and are shown in the following Table.

Additives	RD 17643	RD 18716
1. Chemical Sensitizers	Page 23	Page 648, right column
2. Sensitivity Increasing Agents	--	ditto
3. Spectral Sensitizers, Supersensitizers	Pages 23-24	Page 648, right column to page 649, right column
4. Brightening Agents	Page 24	--
5. Antifoggants and Stabilizers	Pages 24-25	Page 649, right column
6. Light Absorbers, Filter Dyes, Ultraviolet Absorbers	Pages 25-26	Page 649, right column to page 650, left column
7. Stain Inhibitors	Page 25, right column	Page 650, left to right columns
8. Dye Image Stabilizers	Page 25	--
9. Hardeners	Page 26	Page 651, left column
10. Binders	Page 26	ditto
11. Plasticizers, Lubricants	Page 27	Page 650, right column
12. Coating Aids, Surfactants	Pages 26-27	ditto
13. Antistatic Agents	Page 27	ditto

Various color couplers can be used to form direct positive color image in the present invention. The color couplers are compounds which are coupled with the oxidation product of aromatic primary amine color developing agents to form or release a dye which is substantially nondiffusing. It is preferred that the color couplers themselves are nondiffusing compounds. Typical examples of useful color couplers include naphthol or phenol compounds, pyrazolone or pyrazoloazole compounds and cyclic or heterocyclic ketomethylene compounds. Examples of these cyan, magneta and yellow couplers which can be used in the present invention include compounds as described in Research Disclosure, No. 17643, page 25, Item VII-D (December, 1978), ibid., No. 18717 (November, 1979), JP-A-62-215272 and the patent specifications cited therein.

Colored couplers, couplers whose forming dye is appropriately diffusing, non-color-forming couplers, DIR couplers which release restrainers by coupling reaction and polymerized couplers can be used to correct unnecessary absorption in the region of short wavelength which the formed dye has.

Gelatin is advantageous as a binder or protective colloid which can be used for the emulsion layers and intermediate layers of the photographic material of the present invention. In addition, other hydrophilic colloids can be used.

The photographic material of the present invention may contain antifogging agents and color mixing inhibitors. Typical examples thereof are described in JP-A-62-215272 (pages 185 to 193).

Supersensitizing agents can be used in the present invention to improve the color forming properties of the couplers. Typical examples of such compounds include those described in JP-A-62-215272 (pages 121 to 125).

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

Couplers which release photographically useful residues on coupling can be used in the present invention. Preferred DIR couplers which release restrainers are described in the patent specifications cited in RD, 17643, Item VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248 and U.S. Patent 4,248,962.

The couplers of the present invention can be incorporated in the photographic material using conventional dispersion methods.

Examples of high boiling solvents which can be used in oil-in-water dispersion methods are described in U.S. Patent 2,322,027.

The stages and effects of dispersion methods using latexes and examples of latexes used for impregnation are described in U.S. Patent 4,199,363, West German Patent Application Nos. (OLS) 2,541,274 and 2,541,230.

The photographic material of the present invention may contain dyes for preventing irradiation and halation, ultraviolet light absorbers, plasticizers, fluorescent brighteners, matting agents, aerial fog inhibitors, coating aids, hardening agents, antistatic agents, slipperiness improvers and development accelerators in addition to the dyes described above. Typical examples of these additives are described in Research Disclosure, No. 17643, Item VIII-XIII, pages 25 to 27 (December, 1978) and ibid., No. 18716, pages 647 to 651 (November, 1979).

The present invention can be applied to multilayer color photographic materials having at least two different spectral sensitivities provided on a support. Multilayer color photographic materials comprise generally at least one of each of a red-sensitive emulsion layer, a green-sensitive emulsion layer and a blue-sensitive emulsion layer provided on a support. The order of these layers may be arbitrarily changed. Preferably, these layers are arranged in order of a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer from the support or in order of a green-sensitive layer, a red-sensitive layer and a blue-sensitive layer from the support. Each emulsion layer may comprise two or more layers having different sensitivity. A nonsensitive layer may be interposed between two or more emulsion layers having the same color sensitivity. Generally, the red-sensitive layer contains a cyan-forming coupler, the green-sensitive emulsion layer contains a magenta-forming coupler and the blue-sensitive emulsion layer contains a yellow-forming coupler.

It is preferred for the photographic material of the present invention to have auxiliary layers such as a protective layer, an intermediate layer, a filter layer, an antihalation layer, a back layer, a white color reflecting layer, etc., in addition to the silver halide emulsion layers.

The photographic emulsion layers and other layers of the photographic material of the present invention are coated on a support as described in Research Disclosure, No. 17643, Item V-VII, page 28 (December, 1978), European Patent 0102253 or JP-A-61-97655. Further, coating methods as described in Research Disclosure, No. 17643, Item XV, pages 28 and 29 can be used.

The present invention can be applied to various color photographic materials. For example, the present invention can be used in the fields of color reversal papers, color autopositive papers, color reversal films, color autopositive films, color diffusion transfer reversal papers (films), silver dye bleach process (film/papers), and dry silver color papers (films).

In the present invention, the fogging treatment is carried out using a light fogging method and/or a chemical fogging method. Overall surface exposure, that is, fogging exposure in the light fogging method, is carried out after imagewise exposure and/or during development. The imagewise exposed photographic material is exposed in a developing solution, or immersed in the previous bath of the developing solution. Alternatively, the imagewise exposed material is removed from these solutions and exposed before the material is dried. It is most preferred that the exposure be conducted in the developing solution.

Any light sources within the light-sensitive wavelengths of the photographic materials can be used as a light source for the fogging exposure. Generally, a fluorescent lamp, a tungsten lamp, a xenon lamp, a sunlamp, etc., can be used. Specific methods are described in British Patent 1,151,363, JP-B-45-12710, JP-B-45-12709, JP-B-58-6936, JP-A-48-9727, JP-A-56-137350, JP-A-57-129438, JP-A-58-62652, JP-A-58-60739, JP-A-58-70223 (corresponding to U.S. Patent 4,440,851) and JP-A-58-120248 (corresponding to European Patent 89101A2). Light sources having a high color rendering (near white color, if possible) as described in JP-A-56-137350 or JP-A-58-70223 are suitable for photographic materials with sensitivity to light in all wave ranges, for example, color photographic materials. The illuminance of light is in the range of 0.01 to 2,000 lux, preferably 0.05 to 30 lux, more preferably 0.05 to 5 lux. Lower illuminance is preferred for photographic materials containing higher sensitivity emulsions. The adjustment of illuminance may be made by changing the luminous intensity of the light source, reducing the intensity of light through filters or changing the distance between the photographic material and the light source or the angle therebetween. It is possible that the illuminance of the fogging light is increased continuously or stepwise from lower illuminance to higher-illuminance.

It is preferred for the photographic material to be immersed in the developing solution or a solution in the previous bath to thereby allow the solution to penetrate thoroughly into the photographic material and light irradiation is then conducted. The time taken for the light fogging exposure after the penetration of the solution is in the range of generally 2 seconds to 2 minutes, preferably 5 seconds to 1 minute, more preferably 10 seconds to 30 seconds.

The exposure time for fogging is generally 0.01 second to 2 minutes, preferably 0.1 second to 1 minute, more preferably 1 second to 40 seconds.

Nucleating agents which are used in the chemical fogging method can be incorporated in the photographic materials or in the processing solutions for the photographic materials in the present invention.

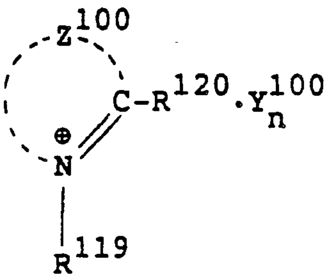
The term "nucleating agent" as used herein refers to substances which react in the surface development of the internal latent image type silver halide emulsion previously not fogged to form a direct positive image. It is particularly preferred in the present invention that the fogging treatment be carried out by using the nucleating agents.

When the nucleating agents are incorporated in the photographic materials, it is preferred to add them to an internal latent image type silver halide emulsion. If desired, the agents may be added to other layers such as an intermediate layer, an undercoat layer and a back layer so long as the nucleating agents are diffused during coating or processing and allowed to be adsorbed by silver halide.

When the nucleating agents are added to the processing solutions, they may be present in the developing solution or in a previous bath having a low pH as described in JP-A-58-178350.

The nucleating agents may be used either alone or as a combination of two or more of them.

The following compounds represented by the following general formulae (N-I) and (N-II) are preferred as the nucleating agents for use in the present invention.



(N-I)

wherein Z^{100} represents a nonmetallic atomic group required for the formation of a 5-membered or 6-membered heterocyclic group which may be optionally substituted; R^{119} represents an aliphatic group; R^{120} represents a hydrogen atom, an aliphatic group or an aromatic group; R^{119} or R^{120} may be optionally substituted; R^{120} may combine together with the heterocyclic ring formed by Z^{100} to form a ring; at least one of R^{119}, R^{120} and Z^{100} has an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or R^{119} and R^{120} form a 6-membered ring to thereby form a dihydropyridinium skeleton; at least one of R^{119}, R^{120} and Z^{100} may have an accelerating group for adsorption to silver halide; Y^{100} is a counter ion for electric charge balance; and n represents 0 or 1.

Examples of suitable compounds having the formula (N-I) include the following compounds.

(N-I- 1): 5-Ethoxy-2-methyl-1-propargylquinolinium bromide
(N-I- 2): 2,4-Dimethyl-1-propargylquinolinium bromide
(N-I- 3): 3,4-Dimethyldihydropyrido[2,1-b]benzothiazolium bromide
(N-I- 4): 6-Ethoxythiocarbonylamino-2-methyl-1-propargylquinolinium trifluoromethanesulfonate
(N-I- 5): 6-(5-Benzotriazolecarboxamido)-2-methyl-1-propargylquinolinium trifluoromethanesulfonate
(N-I- 6): 6-(5-Mercaptotetrazole-1-yl)-2-methyl-1-propargylquinolinium iodide
(N-I- 7): 6-Ethoxythiocarbonylamino-2-(2-methyl-1-propenyl)-1-propargylquinolinium trifluoromethanesulfonate
(N-I- 8): 10-Propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate
(N-I- 9): 7-Ethoxythiocarbonylamino-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate
(N-I- 10): 7-[3-(5-Mercaptotetrazole-1-yl)benzamido]-10-propargyl-1,2,3,4-tetrahydroacridinium perchlorate
(N-I- 11): 7-(5-Mercaptotetrazole-1-yl)-9-methyl-10-propargyl-1,2,3,4-tetrahydroacridinium bromide
(N-I- 12): 7-Ethoxythiocarbonylamino-10-propargyl-1,2-dihydroacridinium trifluoromethanesulfonate
(N-I- 13): 10-Propargyl-7-[3-(1,2,3,4-thiatriazole-5-ylamino)benzamido]-1,2,3,4-tetrahydroacridinium perchlorate
(N-I- 14): 7-(3-Cyclohexylmethoxythiocarbonylaminobenzamido)-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate
(N-I- 15): 7-(3-Ethoxythiocarbonylaminobenzamido)-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate
(N-I- 16): 7-[3-(3-Ethoxythiocarbonylaminophenyl)ureido]-10-propargyl-1,2,3,4-tetrahydroacridinium

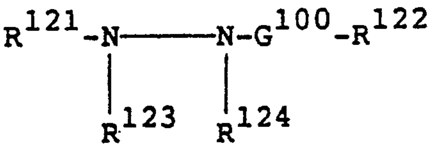
trifluoromethanesulfonate

(N-I- 17): 7-(3-Ethoxythiocarbonylaminobenzenesulfonamido)-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate

(N-I- 18): 7-[3-{3-[3-(5-Mercaptotetrazole-1-yl)phenyl]ureido}benzamido]-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate

(N-I- 19): 7-[3-(5-Mercapto-1,2,3,4-thiadiazole-1-ylamino)benzamido]-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate

(N-I- 20): 7-[3-(3-Butylthioureido)benzamido]-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate



$$R^{121}-\underset{\displaystyle R^{123}}{\underset{|}{N}}-\underset{\displaystyle R^{124}}{\underset{|}{N}}-G^{100}-R^{122}$$

(N-II)

wherein R^{121} represents an aliphatic group, an aromatic group or a heterocyclic group; R^{122} represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, an aryloxy group or an amino group; G^{100} represents a carbonyl group, a sulfonyl group, a sulfoxy group, a phosphoryl group or an iminomethylene group ($NH=C<$); and R^{123} and R^{124} are both a hydrogen atom or one of them is a hydrogen atom and the other is an alkylsulfonyl group, an arylsulfonyl group or an acyl group; and a hydrazone structure ($>N-N=C<$) may be formed by a combination of G^{100}, R^{122}, R^{124} and hydrazine nitrogen. These groups may be optionally substituted.

Examples of compounds having the formula (N-II) include the following compounds.

(N-II- 1): 1-Formyl-2-{4-[3-(2-methoxyphenyl)ureido]phenyl}hydrazine

(N-II- 2): 1-Formyl-2-{4-[3-{3-[3-(2,4-di-tert-pentylphenoxy)propyl]ureido}phenylsulfonylamino]-phenyl}hydrazine

(N-II- 3): 1-Formyl-2-{4-[3-(5-mercaptotetrazole-1-yl)benzamido]phenyl}hydrazine

(N-II- 4): 1-Formyl-2-[4-{3-[3-(5-mercaptotetrazole-1-yl)phenyl]ureido}phenyl]hydrazine

(N-II- 5): 1-Formyl-2-[4-{3-[N-(5-mercapto-4-methyl-1,2,4-triazole-3-yl)carbamoyl]propanamido}phenyl]-hydrazine

(N-II- 6): 1-Formyl-2-{4-[3-{N-[4-(3-mercapto-1,2,4-triazole-4-yl)phenyl]carbamoyl}propanamido]-phenyl}hydrazine

(N-II- 7): 1-Formyl-2-[4-{3-[N-(5-mercapto-1,3,4-thiadiazole-2-yl)carbamoyl]propanamido}phenyl]hydrazine

(N-II- 8): 2-[4-(Benzotriazole-5-carboxamido)phenyl]-1-formylhydrazine

(N-II- 9): 2-[4-{3-[N-(benzotriazole-5-carboxamido)carbamoyl]propanamido}phenyl]-1-formylhydrazine

(N-II-10): 1-Formyl-2-{4-[1-(N-phenylcarbamoyl)thiosemicarbazido]phenyl}hydrazine

(N-II-11): 1-Formyl-2-{4-[3-(3-phenylthioureido)benzamido]phenyl}hydrazine

(N-II-12): 1-Formyl-2-[4-(3-hexylureido)phenyl]hydrazine

(N-II-13): 1-Formyl-2-{4-[3-(5-mercaptotetrazole-1-yl)benzenesulfonamido]phenyl}hydrazine

(N-II-14): 1-Formyl-2-{4-[3-{3-(5-mercaptotetrazole-1-yl)phenyl]ureido}benzenesulfonamido]-phenyl}hydrazine

(N-II-15): 1-Formyl-2-[4-{3-[3-(2,4-di-tert-pentylphenoxy)propyl]ureido}phenyl]hydrazine

The nucleating agents may be incorporated in the photographic materials or the processing solutions for the photographic materials. However, it is preferred for the nucleating agents to be incorporated in the photographic materials.

When the nucleating agents are incorporated in the photographic materials, it is preferred that the agents are added to the internal latent image type silver halide emulsion layers. However, the agents may be added to other layers, such as an intermediate layer, an undercoat layer and a back layer, so long as the nucleating agents are diffused during coating or processing and are adsorbed by silver halide. When the nucleating agents are to be added to the processing solutions, the agents may be present in the developing solution or the previous bath having a low pH as described in JP-A-58-178350.

When the nucleating agents are added to the photographic materials, the agents are used in an amount of preferably 10^{-8} to 10^{-2} mol, particularly 10^{-7} to 10^{-3} mol per mol of silver halide.

When the nucleating agents are added to the processing solutions, the agents are used in any amount of preferably 10^{-5} to 10^{-1} mol/liter, more preferably 10^{-4} to 10^{-2} mol/liter.

The following nucleating accelerators can be used in the present invention to accelerate the function of the nucleating agents.

Tetraazaindenes, triazaindenes and pentaazaindenes, these indenes having at least one mercapto group which may be optionally substituted by an alkali metal or ammonium group can be used as the nucleating accelerators. Further, the compounds described in JP-A-63-106656 (pp. 6 to 16) can be used.

Examples of the nucleating accelerators include, but are not limited to, the following compounds.

(A- 1): 3-Mercapto-1,2,4-triazolo[4,5-a]pyridine
(A- 2): 3-Mercapto-1,2,4-triazolo[4,5-a]pyrimidine
(A- 3): 5-Mercapto-1,2,4-triazolo[1,5-a]pyrimidine
(A- 4): 7-(2-Dimethylaminoethyl)-5-mercapto-1,2,4-triazolo[1,5-a]pyrimidine
(A- 5): 3-Mercapto-7-methyl-1,2,4-triazolo[4,5-a]pyrimidine
(A- 6): 3,6-Dimercapto-1,2,4-triazolo[4,5-b]pyridazine
(A- 7): 2-Mercapto-5-methylthio-1,3,4-thiadiazole
(A- 8): 3-Mercapto-4-methyl-1,2,4-triazole
(A- 9): 2-(3-Dimethylaminopropylthio)-5-mercapto-1,3,4-thiadiazole-hydrochloride
(A- 10): 2-(2-Morpholinoethylthio)-5-mercapto-1,3,4-thiadiazole hydrochloride

The nucleating accelerators may be incorporated in the photographic materials or the processing solutions. It is preferred for the nucleating accelerators to be incorporated in the internal latent image type silver halide emulsion layers or hydrophilic colloid layers (e.g., an intermediate layer, a protective layer) of the photographic materials. It is particularly preferred for the accelerators to be incorporated in the silver halide emulsion layers or layers adjacent thereto.

The color developing solutions which can be used for the development of the photographic materials in the present invention are preferably aqueous alkaline solutions mainly containing aromatic primary amine color developing agents. Aminophenol compounds are useful as color developing agents and p-phenylenediamine compounds are preferred as color developing agents. Typical examples thereof include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline and salts thereof such as sulfate, hydrochloride and p-toluenesulfonate. These compounds may be used either alone or as a combination of two or more of them.

Generally, when reversal processing is to be conducted, back-and-white development is first carried out and color development is then carried out. Black-and-white developing solutions may contain conventional developing agents, such as hydroquinones (e.g., dihydroxybenzenes), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone) and aminophenols (e.g., N-methyl-p-aminophenol). These developing agents may be used either alone or as a combination of two or more of them.

The pH of the color developing solutions and the black-and-white developing solutions is generally in the range of 9 to 12. The replenishment rate of these developing solutions varies depending on the types of color photographic materials, but is usually not more than 3 liters per m^2 of the photographic material. The replenishment rate can be reduced to 500 ml or less when the concentration of bromide ion in the replenisher is reduced.

After color development, the photographic emulsion layer is generally bleached. Bleaching may be carried out simultaneously with fixing (bleaching-fixing treatment) or they can be separately carried out. After bleaching, a bleaching-fixing treatment may be conducted to expedite processing. Treatment may be conducted with a bleach-fixing bath composed of two consecutive tanks. Fixing may conducted before the bleaching-fixing treatment. After the bleaching-fixing treatment, bleaching may be conducted depending on the purpose. Examples of bleaching agents include compounds of polyvalent metals such as iron(III), cobalt(III), chromium(VI) and copper(II), peracids, quinones and nitro compounds.

Examples of fixing agents include thiosulfates, thiocyanates, thioether compounds, thioureas and various iodides. The thiosulfates are widely used as the fixing agents. Particularly, ammonium thiosulfate is most widely used. Sulfites, bisulfites and carbonyl bisulfite adducts are preferred as preservatives for the bleaching-fixing solutions.

Usually, the positive working silver halide color photographic materials of the present invention are subjected to washing and/or stabilization stage after desilverization. The amount of rinsing water in the washing stage varies widely depending on the characteristics (e.g., depending on materials used such as couplers) of the photographic materials, use, the temperature of the rinsing water, the number of rinsing tanks (the number of stages), replenishing system (countercurrent, direct flow) and other conditions. The relationship between the amount of water and the number of rinsing tanks in the multistage countercurrent system can be determined by the method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, pages 248 to 253 (May, 1955).

The color developing agents may be incorporated in the positive working silver halide color photographic materials of the present invention for the purpose of simplifying and expediting processing. It is preferred for precursors of color developing agents to be used when they are incorporated in the photographic materials.

Conventional developing agents can be used for the development of black-and-white photographic materials in the present invention. Examples of the developing agents include polyhydroxybenzenes such as hydroquinone, 2-chlorohydroquinone, 2-methylhydroquinone, catechol and pyrogallol; aminophenols such as p-aminophenol, N-methyl-p-aminophenol and 2,4-diaminophenol; 3-pyrazolidones such as 1-phenyl-3-pyrazolidones, 1-phenyl-4,4′-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone and 5,5-dimethyl-1-phenyl-3-pyrazolidone; and ascorbic acids. These compounds may be used either alone or as a combination of two or more of them. The developing solution described in JP-A-58-55928 can also be used.

The present invention is now illustrated in greater detail by reference to the following examples which, however, are not to be construed as limiting the present invention in any way.

EXAMPLE 1

A paper support (thickness: 100 µm, both sides thereof being laminated with polyethylene) was coated with the following first to fourteenth layers and the back thereof was coated with the following fifteenth and sixteenth layers to prepare a multilayer color photographic material. Polyethylene on the side of the first layer to be coated contained titanium oxide as a white pigment and a very small amount of ultramarine as a bluing dye (the chromaticity of the surface of the support was 88.0, -0.20, -0.75 in L^*, a^*, b^*, system).

Composition of Sensitive Layers

The following components in the following coating weights (unit: g/m^2) were used. The amount of silver halide is represented as a coating weight in terms of silver. The emulsions used in each layer were prepared according to the method of preparation of Emulsion EMI. As the emulsion of the fourteenth layer, a Lippmann emulsion which was not subject to surface chemical sensitization was used.

First Layer: Antihalation Layer	
Black Colloidal Silver	0.10
Gelatin	0.70

Second Layer: Intermediate Layer	
Gelatin	0.70

Third Layer: Low Sensitivity Red-Sensitive Layer	
Silver Bromide (mean grain size: 0.25 µm, size distribution (coefficient of variation): 8%, octahedral) Spectrally Sensitized with Red-Sensitizing Dyes (ExS-1, ExS-2, ExS-3)	0.04
Silver Chlorobromide (silver chloride: 5 mol%, mean grain size: 0.40 µm, size distribution: 10%, octahedral) Spectrally Sensitized with Red-Sensitizing Dyes (ExS-1, ExS-2, ExS-3)	0.08
Gelatin	1.00
Cyan Coupler (ExC-1, ExC-2, ExC-3 in a ratio of 1/1/0.2)	0.30
Antifading Agent (Cpd-1, Cpd-2, Cpd-3, Cpd-4 in equal amounts by weight)	0.18
Stain Inhibitor (Cpd-5)	0.003
Dispersion Medium (Cpd-6) for Coupler	0.03
Solvent (Solv-1, Solv-2, Solv-3 in equal amounts by weight) for Coupler	0.12

Fourth Layer: High Sensitivity Red-Sensitive Layer	
Silver Bromide (mean grain size: 0.60 µm, size distribution: 15%, octahedral) Spectrally Sensitized with Red-Sensitizing Dyes (ExS-1, ExS-2, ExS-3)	0.14
Gelatin	1.00
Cyan Coupler (ExC-1, ExC-2, ExC-3 in a weight ratio of 1/1/0.2)	0.30
Antifading Agent (Cpd-1, Cpd-2, Cpd-3, Cpd-4 in equal amounts)	0.18
Dispersion Medium (Cpd-6) for Coupler	0.03
Solvent (Solv-1, Solv-2, Solv-3 in equal amounts by weight) for Coupler	0.12

Fifth Layer: Intermediate Layer	
Gelatin	1.00
Color Mixing Inhibitor (Cpd-7)	0.08
Solvent (Solv-4, Solv-5 in equal amounts by weight) for Color Mixing Inhibitor	0.16
Polymer Latex (Cpd-8)	0.10

Sixth Layer: Low Sensitivity Green-Sensitive Layer	
Silver Bromide (mean grain size: 0.25 µm, size distribution: 8%, octahedral) Spectrally Sensitized with Green-Sensitizing Dye (ExS-4)	0.04
Silver Chlorobromide (silver chloride: 5 mol%, mean grain size: 0.40 µm, size distribution: 10%, octahedral) Spectrally Sensitized with Green-Sensitizing Dye (ExS-4)	0.06
Gelatin	0.80
Magenta Coupler (ExM-1, ExM-2, ExM-3 in equal amounts by weight)	0.11
Antifading Agent (Cpd-9, Cpd-26 in equal amounts by weight)	0.15
Stain Inhibitor (Cpd-10, Cpd-11, Cpd-12, Cpd-13 in a ratio of 10/7/7/1)	0.025
Dispersion Medium (Cpd-6) for Coupler	0.05
Solvent (Solv-4, Solv-6 in equal amounts by weight) for Coupler	0.15

Seventh Layer: High Sensitivity Green-Sensitive Layer	
Silver Bromide (mean grain size: 0.65 µm, size distribution: 16%, octahedral) Spectrally Sensitized with Green-Sensitizing Dye (ExS-4)	0.10
Gelatin	0.80
Magenta Coupler (ExM-1, ExM-2, ExM-3 in equal amounts by weight)	0.11
Antifading Agent (Cpd-9, Cpd-26 in equal amounts by weight)	0.15
Stain Inhibitor (Cpd-10, Cpd-11, Cpd-12, Cpd-13 in a weight ratio of 10/7/7/1)	0.025
Dispersion Medium (Cpd-6) for Coupler	0.05
Solvent (Solv-4, Solv-6 in equal amounts) for Coupler	0.15

Eighth Layer: Intermediate Layer

The same as the Fifth Layer

Ninth Layer: Yellow Filter Layer	
Yellow Colloidal Silver	0.12
Gelatin	0.07
Color Mixing Inhibitor (Cpd-7)	0.03
Solvent (Solv-4, Solv-5 in equal amounts by weight) for Color Mixing Inhibitor	0.10
Polymer Latex (Cpd-8)	0.07

Tenth Layer: Intermediate Layer

The same as the Fifth Layer

Eleventh Layer: Low Sensitivity Blue-Sensitive Layer	
Silver Bromide (mean grain size: 0.40 µm, size distribution: 8%, octahedral) Spectrally Sensitized with Blue-Sensitizing Dyes (ExS-5, ExS-6)	0.07
Silver Chlorobromide (silver chloride: 8 mol%, mean grain size: 0.60 µm, size distribution: 11%, octahedral) Spectrally Sensitized with Blue-Sensitizing Dyes (ExS-5, ExS-6)	0.14
Gelatin	0.80
Yellow Coupler (ExY-1, ExY-2 in equal amounts by weight)	0.35
Antifading Agent (Cpd-14)	0.10
Stain Inhibitor (Cpd-5, Cpd-15 in a ratio of 1/5)	0.007
Dispersion Medium (Cpd-6) for Coupler	0.05
Solvent (Solv-2) for Coupler	0.10

Twelfth Layer: High Sensitivity Blue-Sensitive Layer	
Silver Bromide (mean grain size: 0.85 µm, size distribution: 18%, octahedral) Spectrally Sensitized with Blue-Sensitizing Dyes (ExS-5, ExS-6)	0.15
Gelatin	0.60
Yellow Coupler (ExY-1, ExY-2 in equal amounts)	0.30
Antifading Agent (Cpd-4)	0.10
Stain Inhibitor (Cpd-5, Cpd-15 in a weight ratio of 1/5)	0.007
Dispersion Medium (Cpd-6) for Coupler	0.05
Solvent (Solv-2) for Coupler	0.10

Thirteenth Layer: Ultraviolet Light Absorbing Layer	
Gelatin	1.00
Ultraviolet Light Absorber (Cpd-2, Cpd-4, Cpd-16 in equal amounts)	0.50
Color Mixing Inhibitor (Cpd-7, Cpd-17 in equal amounts by weight)	0.03
Dispersion Medium (Cpd-6)	0.02
Solvent (Solv-2, Solv-7 in equal amounts by weight) for Ultraviolet Light Absorber	0.08
Irradiation Preventing Dye (Cpd-18, Cpd-19, Cpd-20, Cpd-21 in a weight ratio of 10/10/13/15)	0.05

Fourteenth Layer: Protective Layer	
Fine Grain of Silver Chlorobromide (silver chloride: 97 mol%, mean grain size: 0.1 µm)	0.03
Acrylic-Modified Copolymer of Polyvinyl Alcohol	0.01
Polymethyl Methacrylate Particles (average particle size: 2.4 µm) and Silicon Oxide (average particle size: 5 µm) (in equal amounts)	0.05
Gelatin	1.80
Hardener (H-1, H-2 in equal amounts by weight) for Gelatin	0.18

Fifteenth Layer: Back Layer	
Gelatin	2.50
Ultraviolet Light Absorber (Cpd-2, Cpd-4, Cpd-16 in equal amounts by weight)	0.50
Dye (Cpd-18, Cpd-19, Cpd-20, Cpd-21 in equal amounts by weight)	0.06

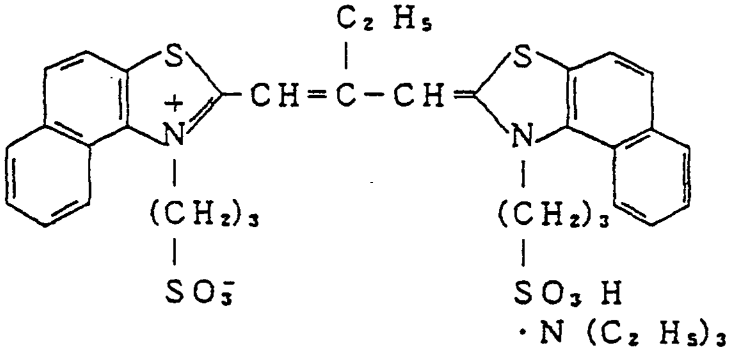
Sixteenth Layer: Protective Layer for Back	
Polymethyl Methacrylate Particles (average particle size: 2.4 µm) and Silicon Oxide (average particle size: 5 µm) (in equal amounts)	0.05
Gelatin	2.00
Hardener (H-1, H-2 in equal amounts by weight) for Gelatin	0.14

Preparation of Emulsion EMI

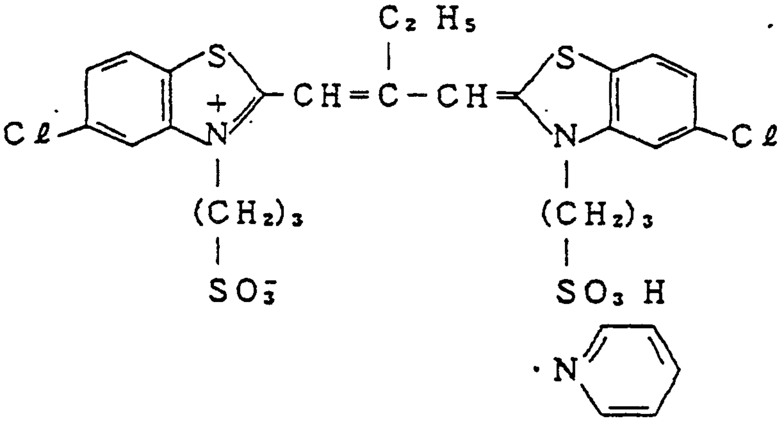
An aqueous solution of silver nitrate and potassium bromide were simultaneously added to an aqueous gelatin solution with vigorous stirring at 75 °C over a period of 15 minutes to obtain octahedral silver bromide grains having a mean grain size of 0.40 µm. 0.3 g of 3,4-dimethyl-1,3-thiazoline-2-thione, 6 mg of sodium thiosulfate and 7 mg of chloroauric acid (tetrahydrate) in order were added to the emulsion, each amount being per mol of silver. The emulsion was heated at 75 °C for 80 minutes to carry out chemical sensitization. The thus-obtained grains were grown as a core under the same precipitation conditions as those initially used to obtain finally an octahedral monodisperse core/shell type silver bromide emulsion having a mean grain size of 0.7 µm. The coefficient of variation in grain size was about 10%. 1.5 mg of sodium thiosulfate and 1.5 mg of chloroauric acid (tetrahydrate) were added to the emulsion, each amount being per mol of silver. The emulsion was heated at 60 °C for 60 minutes to carry out chemical sensitization, thus obtaining an internal latent image type silver halide emulsion.

10^{-3} wt% of ExZK-1 and 10^{-2} wt% of ExZK-2 as nucleating agents and 10^{-2} wt% of Cpd-22 as a nucleating accelerator were used for each sensitive layer. Further, Alkanol XC (Du Pont) and sodium alkylbenzenesulfonate as emulsifying dispersion media and succinic ester Magefac F-120 (Dainippon Ink & Chemical Inc.) as a coating aid were used for each layer. Cpd-23, Cpd-24, Cpd-25 as stabilizers were used for the silver halide-containing layers and the colloidal silver-containing layers. The resulting sample was referred to as Sample 1. The following compounds were used in producing Sample 1.

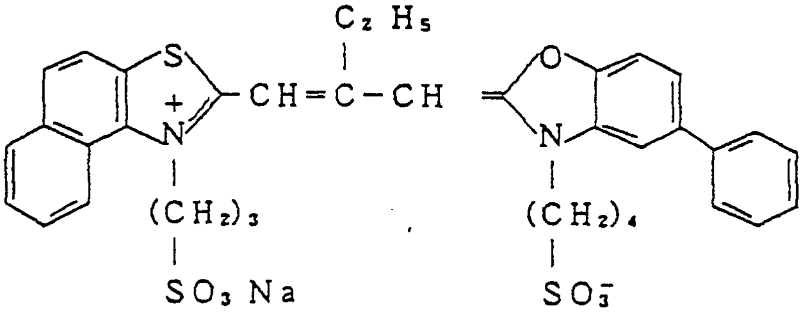
ExS-1



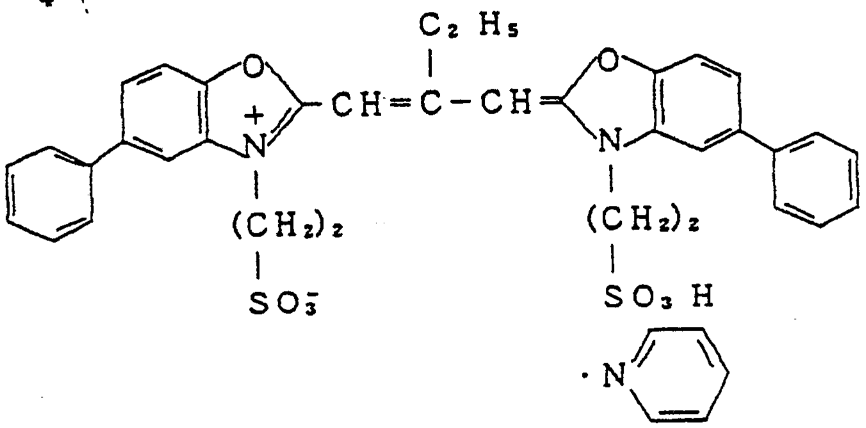
ExS-2



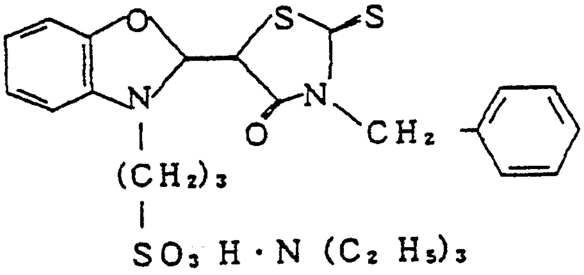
ExS-3



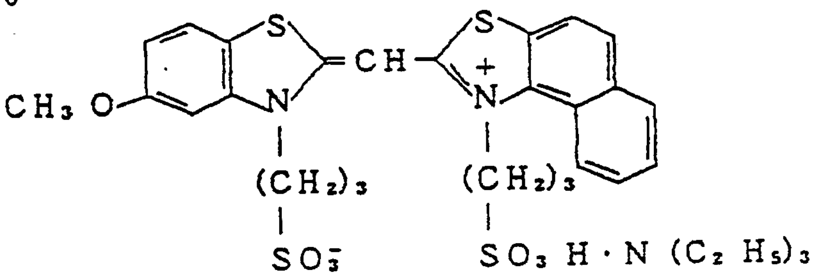
ExS-4



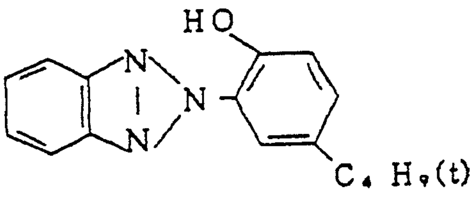
ExS-5



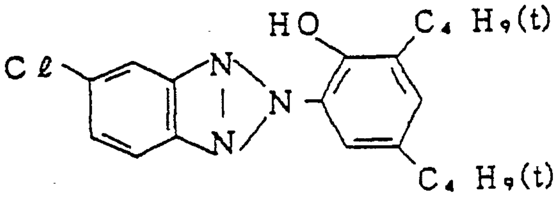
ExS-6



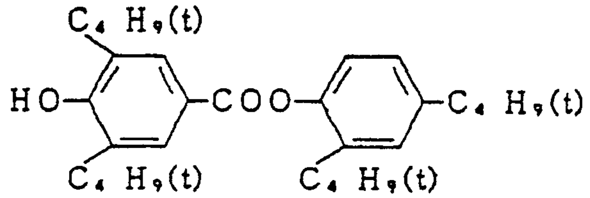
Cpd-1



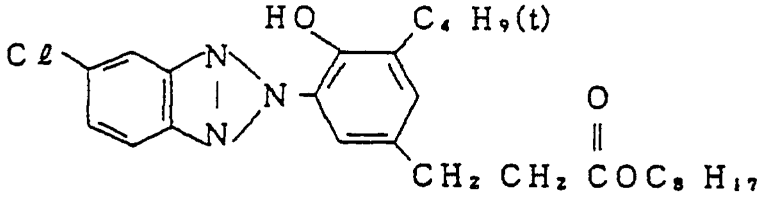
Cpd-2



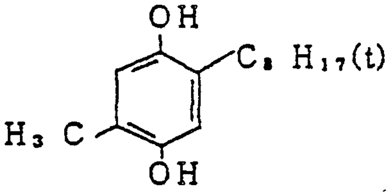
Cpd-3



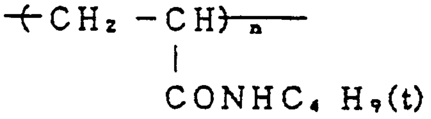
Cpd-4



Cpd-5



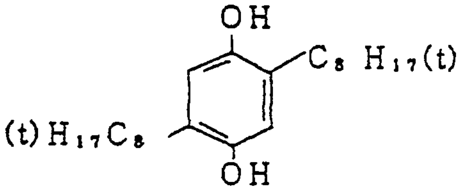
Cpd-6



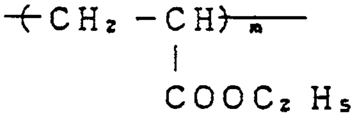
$$\left(CH_2-\underset{\underset{CONHC_4H_9(t)}{|}}{CH}\right)_n$$

n = 100 ~ 1000

Cpd-7

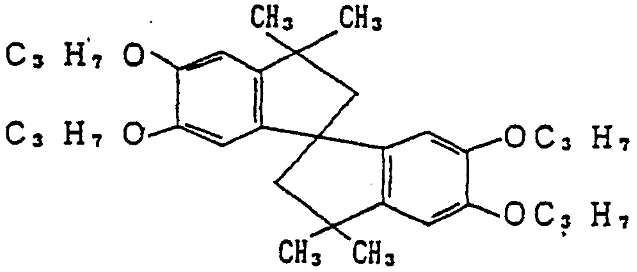


Cpd-8

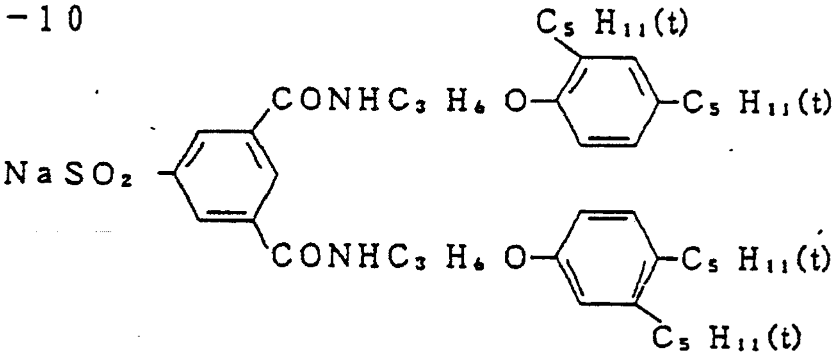


$$\left(CH_2-\underset{\underset{COOC_2H_5}{|}}{CH}\right)_m$$

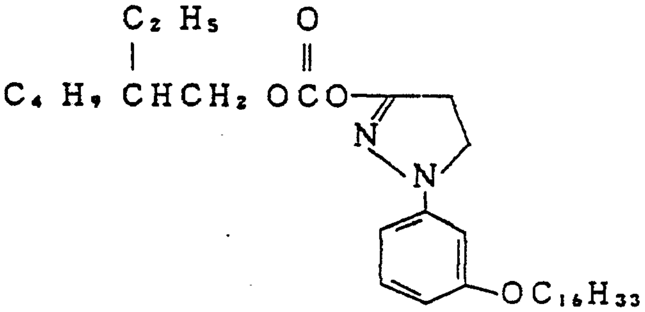
Cpd-9



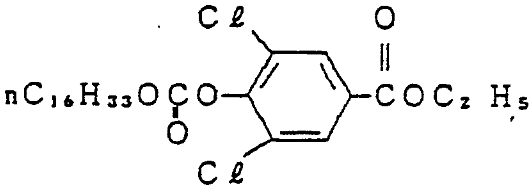
Cpd-10



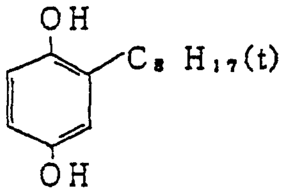
Cpd-11



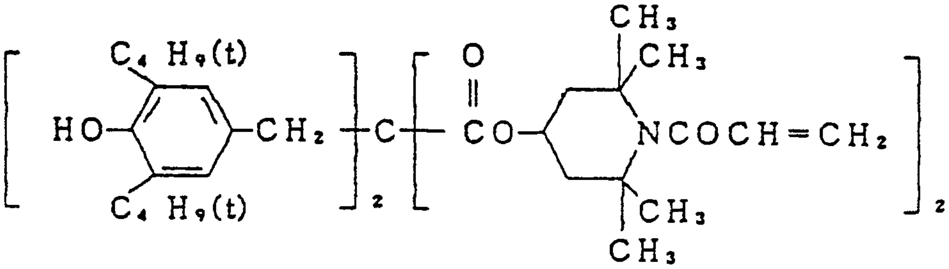
Cpd-12



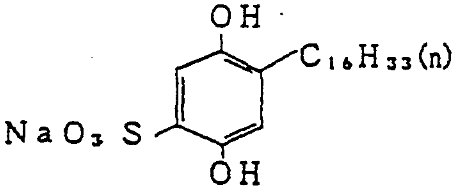
Cpd-13



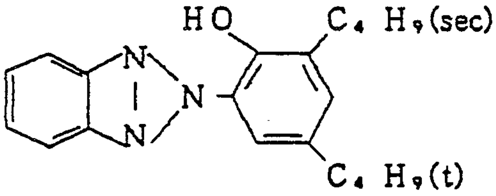
Cpd-14



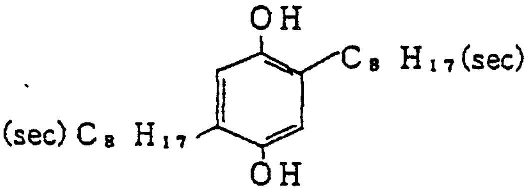
Cpd-15



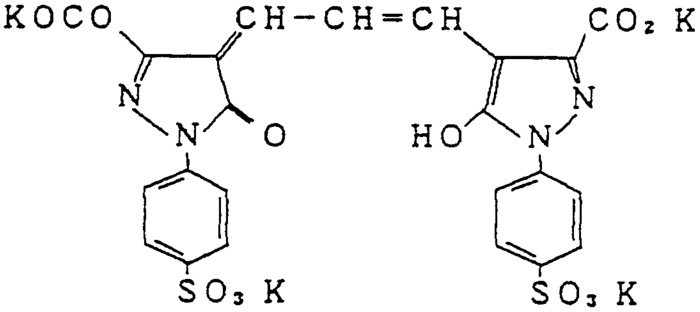
Cpd-16



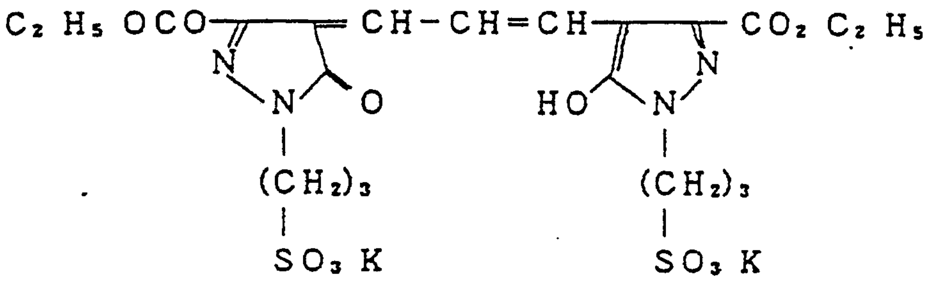
Cpd-17



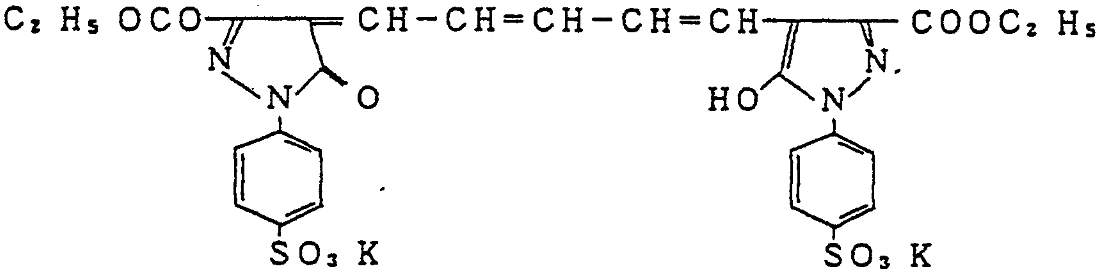
Cpd-18



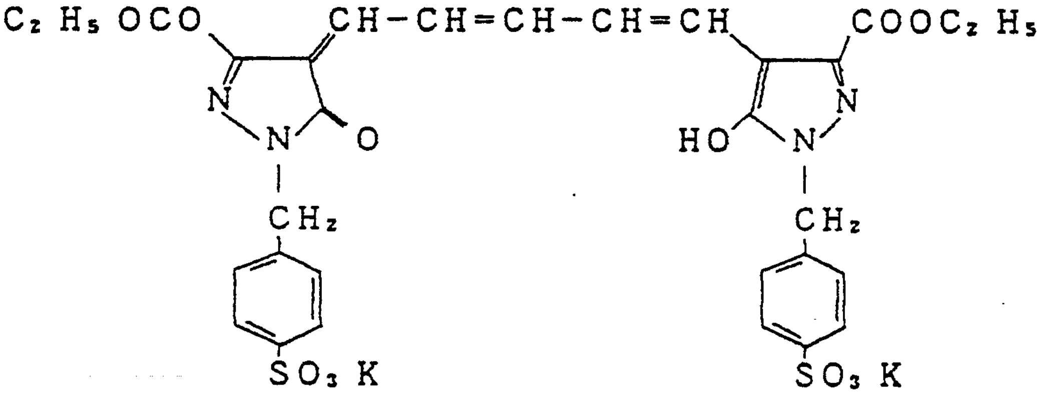
Cpd-19



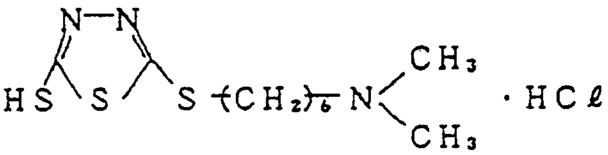
Cpd-20



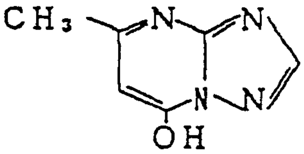
Cpd-21



Cpd−22



Cpd−23



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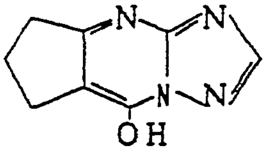
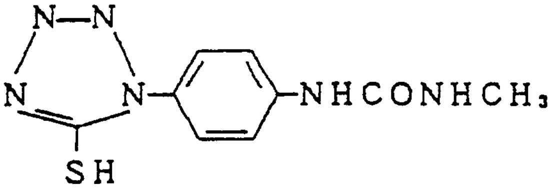
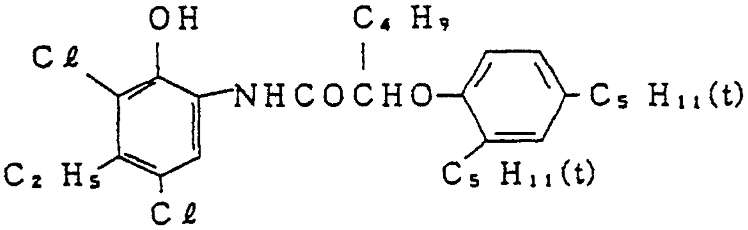


Cpd−25



Cpd−26

ExC−1



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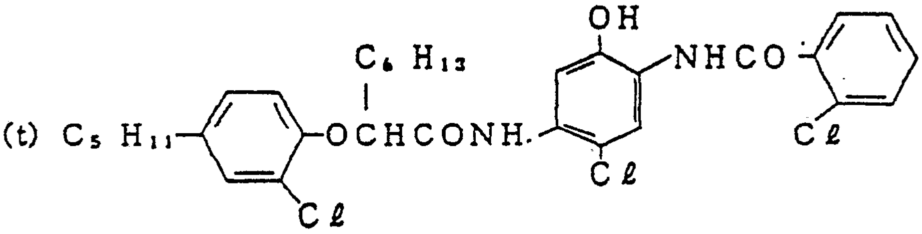
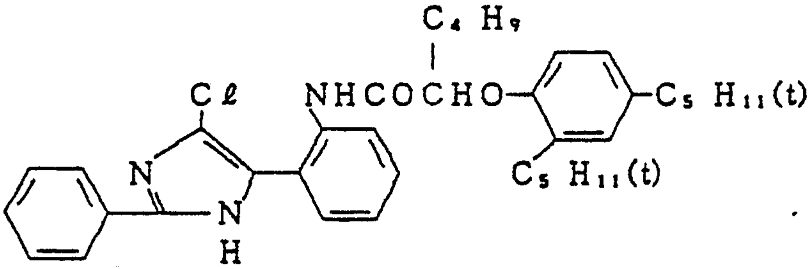


ExC-3



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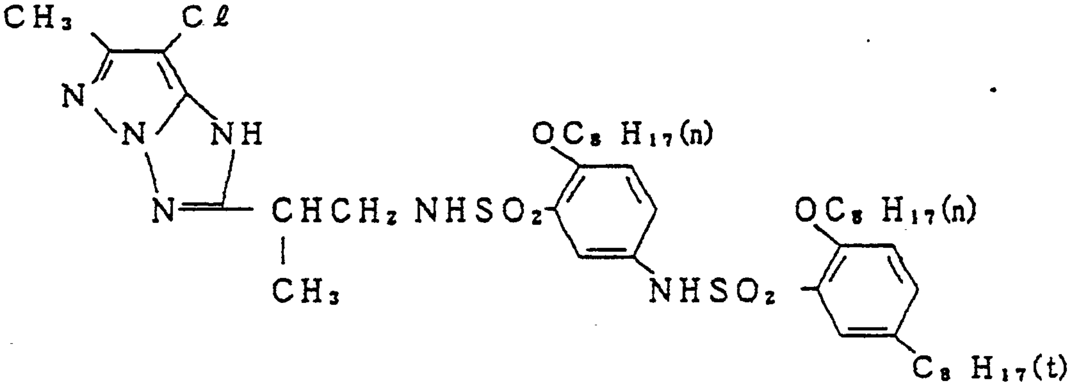

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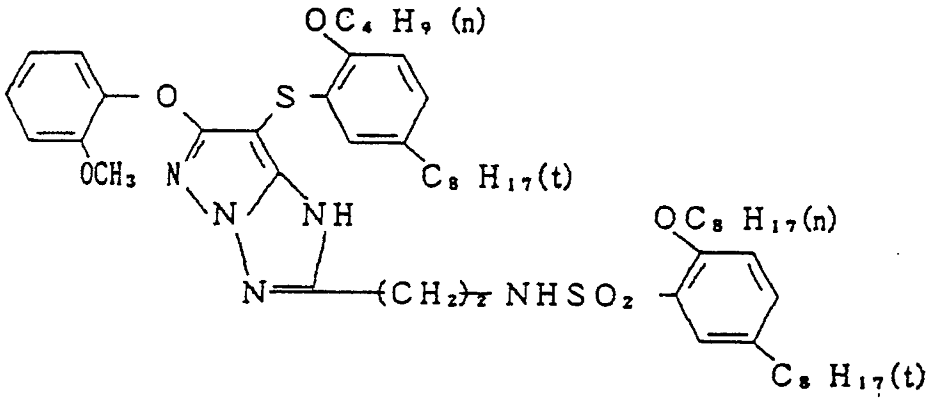

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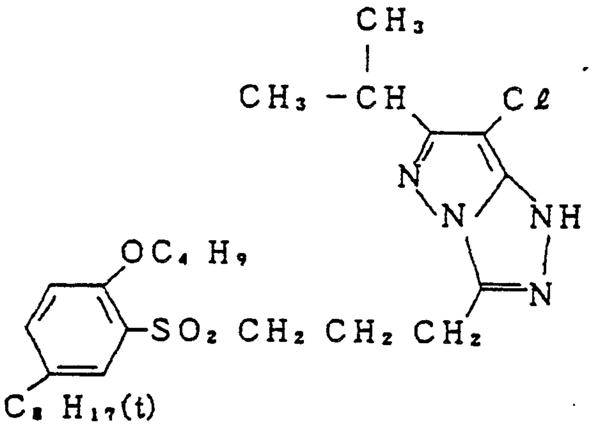
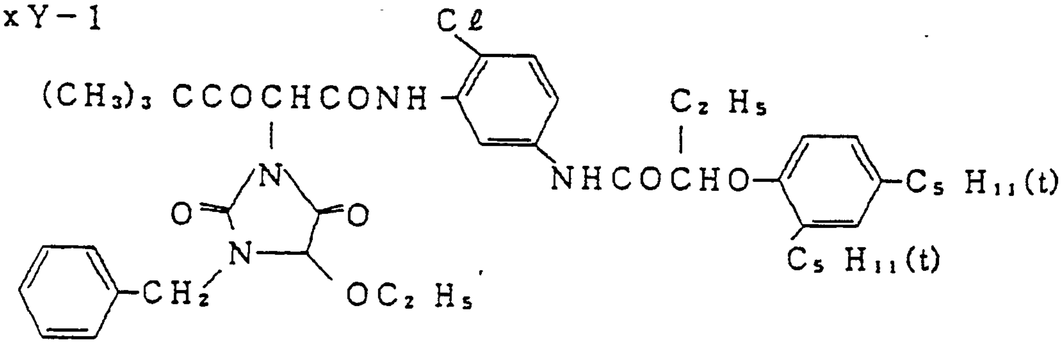
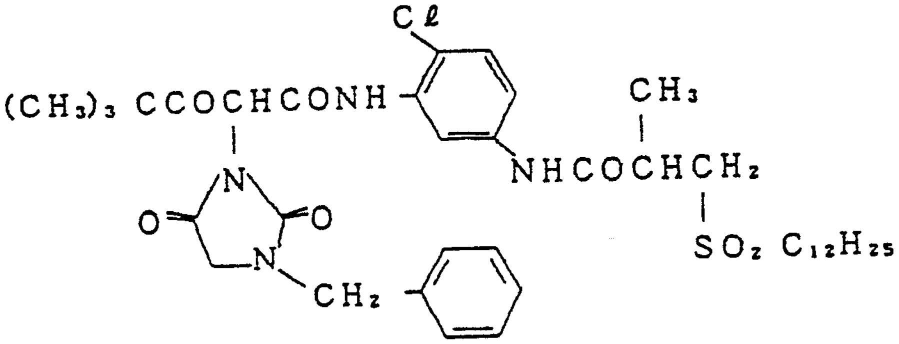


ExY-1



ExY-2



Solv-1 Di(2-ethylhexyl) sebacate
Solv-2 Trinonyl phosphate
Solv-3 Di(3-methylhexyl) phthalate
Solv-4 Tricresyl phosphate
Solv-5 Dibutyl phthalate
Solv-6 Trioctyl phosphate
Solv-7 Di(2-ethylhexyl) phthalate
H-1 1,2-Bis(vinylsulfonylacetamido)ethane
H-2 Na salt of 4,6-dichloro-2-hydroxy-1,3,5-triazine
ExZK-1 7-(3-Ethoxythiocarbonylaminobenzamido)-9-methyl-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate
ExZK-2 2-[4-{3-[3-{3-[5-{3-[2-Chloro-5-(1-dodecyloxycarbonylethoxycarbonyl)phenylcarbamoyl]-4-hydroxy-1-naphthylthio}tetrazol-1-yl]phenyl}ureido]benzenesulfonamido}phenyl]-1-formylhydrazine

Each sample was subjected to a running test using the following processing stages in an automatic processor until the accumulated replenishment rate of the processing solution amounted to three times the tank capacity.

Processing Stage	Time	Temperature	Tank Solution Capacity	Replenishment Rate
	(sec)	(° C)	(liter)	(ml/m²)
Color Development	135	38	15	300
Bleaching-Fixing	40	33	3	300
Rinse (1)	40	33	3	--
Rinse (2)	40	33	3	320
Drying	30	80		

The replenishment system of rinsing water was a countercurrent system such that the rinsing bath (2) was replenished and overflow solution from the rinsing bath (2) was introduced in the rinsing bath (1). The amount of the bleaching-fixing solution brought over from the bleaching-fixing bath to the rinsing bath (1) was 35 ml/m² and the ratio of the replenishment rate of rinsing water to the amount of the bleaching-fixing solution brought over from the bleaching-fixing bath was 9.1.

Each processing solution had the following composition.

Color Developing Solution:		
	Tank Solution	Replenisher
D-Sorbitol	0.15 g	0.20 g
Sodium Naphthalenesulfonate/Formaldehyde Condensate	0.15 g	0.20 g
Ethylenediaminetetrakismethylenephosphonic Acid	1.5 g	1.5 g
Diethylene Glycol	12.0 ml	16.0 ml
Benzyl Alcohol	13.5 ml	18.0 ml
Potassium Bromide	0.80 g	--
Benzotriazole	0.003 g	0.004 g
Sodium Sulfite	2.4 g	3.2 g
N,N-Bis(carboxymethyl)hydrazine	6.0 g	8.0 g
D-Glucose	2.0 g	2.4 g
Triethanolamine	6.0 g	8.0 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate	6.4 g	8.5 g
Potassium Carbonate	30.0 g	25.0 g
Fluorescent Brightener (diaminostilbene type)	1.0 g	1.2 g
Water to make	1,000 ml	1,000 ml
pH (25 °C)	10.25	10.75

Bleaching-Fixing Solution:		
	Tank Solution	Replenisher
Disodium Ethylenediaminetetraacetate Dihydrate	4.0 g	The same as tank solution
Ethylenediaminetetraacetic Acid Fe(III) Ammonium Dihydrate	70.0 g	
Ammonium Thiosulfate (700 g/liter)	180 ml	
Sodium p-Toluenesulfinate	20.0 g	
Sodium Bisulfite	20.0 g	
5-Mercapto-1,3,4-triazole	0.5 g	
Ammonium Nitrate	10.0 g	
Water to make	1,000 ml	
pH (25 °C)	6.20	

Rinsing Water (both tank solution and replenisher)

Tap water was passed through a mixed bed system column packed with an H-type strongly acidic cation exchange resin (Amberlite IR-120B, a product of Rohm & Haas Co.) and an OH-type anion exchange resin (Amberlite IR-400) to reduce the concentration of each of calcium ion and magnesium ion to 3 mg/liter or lower. Subsequently, sodium dichloroisocyanurate (20 mg/liter) and sodium sulfate (1.5 g/liter) were added thereto. The pH of the resulting solution was in the range of 6.5 to 7.5.

Samples 2 to 10 were prepared in the same manner as in the preparation of Sample 1 except that the compounds of the present invention and comparative compound were used in combination with or in place of the irradiation preventing dyes of the Thirteenth Layer of Sample 1. The structures of Samples 2 to 10 are shown in Table 1 below.

The following tests were carried out to evaluate the color reproducibility of the resulting samples. Macbeth color checker was photographed using a color negative film (SHR-100, a product of Fuji Photo Film Co., Ltd.) and printed on color paper (02A, a product of Fuji Photo Film Co., Ltd.) to prepare the original. The original was printed on each of Samples 1 to 10 by using a reflection type printer and development was carried out using the processing stages described above to prepare color prints. The density and color of the prints were adjusted so that a gray patch of neutral 5 of Macbeth color checker on the color paper original became a gray color having a density of 1.0 on the print. Corrective Munsell notation HVC values of color patches red, green and blue of Macbeth color chart on the resulting prints were measured. The C values are shown in Table 1 below. A higher C value means that the color of the sample is reproduced with higher saturation. It was confirmed that large and small values corresponded to the brightness of each color when prints were visually examined.

TABLE 1

Sample No.	Dye Added to 13th Layer and Amount (g/m^2)		Maximum Absorption Wavelength in Gelatin Film (Half Width) (nm)	C Value of Color Patch on Print			Stain after Processing (C Density)
				Red	Green	Blue	
1 (Comparison)	Cpd-18	0.010	550	10.0	8.0	6.2	0.14
	Cpd-19	0.010	567				
	Cpd-20	0.014	668				
	Cpd-21	0.016	666				
2 (Comparison)	Cpd-18	0.025	ditto	10.1	8.2	6.1	0.14
	Cpd-19	0.010					
	Cpd-20	0.014					
	Cpd-21	0.016					
3 (Comparison)	Cpd-18	0.010	ditto	10.0	8.1	6.2	0.14
	Cpd-19	0.010					
	Cpd-20	0.019					
	Cpd-21	0.016					

TABLE 1 (cont'd)

Sample No.	Dye Added to 13th Layer and Amount (g/m^2)		Maximum Absorption Wavelength in Gelatin Film (Half Width) (nm)	C Value of Color Patch on Print			Stain after Processing (C Density)
				Red	Green	Blue	
4 (Invention)	Cpd-18	0.010	550	10.9	8.5	6.4	0.14
	Cpd-19	0.010	567				
	Cpd-20	0.014	668				
	Cpd-21	0.016	666				
	I-2	0.015	620 (75)				
5 (Invention)	Cpd-18	0.010	The same as Sample 1	11.0	8.7	6.3	0.14
	Cpd-19	0.010					
	Cpd-20	0.005					
	Cpd-21	0.005					
	II-2	0.015	624 (45)				

TABLE 1 (cont'd)

Sample No.	Dye Added to 13th Layer and Amount (g/m²)		Maximum Absorption Wavelength in Gelatin Film (Half Width) (nm)	C Value of Color Patch on Print			Stain after Processing (C Density)
				Red	Green	Blue	
6 (Invention)	Cpd-18	0.005	The same as Sample 1	10.5	8.3	7.0	0.14
	Cpd-19	0.005					
	Cpd-20	0.014					
	Cpd-21	0.016					
	III-12	0.012	525 (60)				
7 (Invention)	Cpd-18	0.010	The same as Sample 1	10.6	8.4	6.8	0.14
	Cpd-19	0.010					
	Cpd-20	0.014					
	Cpd-21	0.016					
	IV-2	0.015	514 (58)				

T A B L E 1 (cont'd)

Sample No.	Dye Added to 13th Layer and Amount (g/m^2)		Maximum Absorption Wavelength in Gelatin Film (Half Width) (nm)	C Value of Color Patch on Print			Stain after Processing (C Density)
				Red	Green	Blue	
8 (Invention)	Cpd-18	0.010	The same as Sample 1	10.8	8.5	6.9	0.14
	Cpd-19	0.010					
	Cpd-20	0.014					
	Cpd-21	0.016					
	I-2	0.015	620 (75)				
	IV-2	0.015	514 (58)				
9 (Invention)	Cpd-18	0.005	The same as Sample 1	10.9	8.8	7.0	0.14
	Cpd-19	0.005					
	Cpd-20	0.007					
	Cpd-21	0.008					
	III-12	0.015	525 (60)				
	II-2	0.015	624 (45)				

TABLE 1 (cont'd)

Sample No.	Dye Added to 13th Layer and Amount (g/m^2)		Maximum Absorption Wavelength in Gelatin Film (Half Width) (nm)	C Value of Color Patch on Print			Stain after Processing (C Density)
				Red	Green	Blue	
10 (Invention)	IV-2	0.015	514 (58)	10.6	8.5	6.9	0.14
	IV-9	0.012	615 (72)				

It is clear from the results in Table 1 that Samples 4 to 10 according to the present invention gave an increased C value with respect to any one or all of red, green or blue, provided prints having high saturation and have improved color reproducibility as compared with Comparative Samples 1 to 3.

EXAMPLE 2

A paper support (both sides thereof being laminated with polyethylene) was coated with the following first layer to twelfth layer to prepare a color photographic material (Sample 11). Polyethylene on the side of the first layer contained titanium white as a white pigment and a very small amount of ultramarine as a bluing dye.

Composition of Sensitive Layer

The following components in the following coating weights (unit: g/m^2) were used. The amounts of silver halide are represented as a coating weight in terms of silver.

First Layer: Gelatin Layer	
Gelatin	1.30

Second Layer: Antihalation Layer	
Black Colloidal Silver	0.10
Gelatin	0.70

Third Layer: Low Sensitivity Red-Sensitive Layer	
Silver Iodobromide (silver iodide: 5.0 mol%, mean grain size: 0.4 µm) Spectrally Sensitized with Red-Sensitizing Dyes (*1 and *2)	0.15
Gelatin	1.00
Cyan Coupler (*3)	0.14
Cyan Coupler (*4)	0.07
Antifading Agent (*5, *6 and *7)	0.10
Solvent (*8 and *9) for Coupler	0.06

Fourth Layer: High Sensitivity Red-Sensitive Layer	
Silver Iodobromide (silver iodide: 6.0 mol%, mean grain size: 0.7 µm) Spectrally Sensitized with Red-Sensitizing Dyes (*1 and *2)	0.15
Gelatin	1.00
Cyan Coupler (*3)	0.20
Cyan Coupler (*4)	0.10
Antifading Agent (*5, *6 and *7)	0.15
Solvent (*8 and *9) for Coupler	0.10

Fifth Layer: Intermediate Layer	
Magenta Colloidal Silver	0.02
Gelatin	1.00
Color Mixing Inhibitor (*10)	0.08
Solvent (*11 and *12) for Color Mixing Inhibitor	0.16
Polymer Latex (*13)	0.10

Sixth Layer: Low Sensitivity Green-Sensitive Layer	
Silver Iodobromide (silver iodide: 2.5 mol%, grain size: 0.4 µm) Spectrally Sensitized with Green-Sensitizing Dye (*14)	0.10
Gelatin	0.80
Magenta Coupler (*15)	0.10
Antifading Agent (*16)	0.10
Stain Inhibitor (*17)	0.01
Stain Inhibitor (*18)	0.001
Solvent (*11 and *19) for Coupler	0.15

Seventh Layer: High Sensitivity Green-Sensitive Layer	
Silver Iodobromide (silver iodide: 3.5 mol%, grain size: 0.9 µm) Spectrally Sensitized with Green-Sensitizing Dye (*14)	0.10
Gelatin	0.80
Magenta Coupler (*15)	0.10
Antifading Agent (*16)	0.10
Stain Inhibitor (*17)	0.01
Stain Inhibitor (*18)	0.001
Solvent (*11 and *19) for Coupler	0.15

Eighth Layer: Yellow Filter Layer	
Yellow Colloidal Silver	0.20
Gelatin	1.00
Color Mixing Inhibitor (*10)	0.06
Solvent (*11 and *12) for Color Mixing Inhibitor	0.15
Polymer Latex (*13)	0.10

Ninth Layer: Low Sensitivity Blue-Sensitive Layer	
Silver Iodobromide (silver iodide: 2.5 mol%, grain size: 0.5 µm) Spectrally Sensitized with Blue-Sensitizing Dye (*20)	0.15
Gelatin	0.50
Yellow Coupler (*21)	0.20
Stain Inhibitor (*18)	0.001
Solvent (*9) for Coupler	0.15

Tenth Layer: High Sensitivity Blue-Sensitive Layer	
Silver Iodobromide (silver iodide: 2.5 mol%, grain size: 1.2 µm) Spectrally Sensitized with Blue-Sensitizing Dye (*20)	0.25
Gelatin	1.00
Yellow Coupler (*21)	0.40
Stain Inhibitor (*18)	0.002
Solvent (*9) for Coupler	0.10

Eleventh Layer: Ultraviolet Light Absorbing Layer	
Gelatin	1.50
Ultraviolet Light Absorber (*22, *6 and *7)	1.00
Color Mixing Inhibitor (*23)	0.06
Solvent (*9) for Color Mixing Inhibitor	0.15
Irradiation Preventing Dye (*24)	0.02
Irradiation Preventing Dye (*25)	0.02

Twelfth Layer: Protective Layer	
Fine Grains of Silver Chlorobromide (silver chloride: 97 mol%, mean grain size: 0.2 µm)	0.07
Gelatin	1.50
Hardening Agent (*26) for Gelatin	0.17

*1 Na salt of 5,5′-dichloro-3,3′-di(3-sulfobutyl)-9-ethylthiacarbocyanine

*2 Triethylammonium-3-[2-{2-[3-(3-sulfopropyl)naphtho[1,2-d]thiazoline-2-indenemethyl]-1-butenyl}-3-naphtho[1,2-d]thiazolino]propanesulfonate

*3 2-[α-(2,4-Di-t-amylphenoxy)hexanamido]-4,6-dichloro-5-ethylphenol

*4 2-(2-Chlorobenzoylamido)-4-chloro-5-[α-(2-chloro-4-t-amylphenoxy)octanamido]phenol

*5 2-(2-Hydroxy-3-sec-5-t-butylphenyl)benzotriazole

*6 2-(2-Hydroxy-5-t-butylphenyl)benzotriazole

*7 2-(2-Hydroxy-3,5-di-t-butylphenyl)-6-chlorobenzotriazole

*8 Di(2-ethylhexyl) phthalate

*9 Trinonyl phosphate

*10 2,5-Di-t-octylhydroquinone

*11 Tricresyl phosphate

*12 Dibutyl phthalate

*13 Polyethyl acrylate

*14 Na salt of 5,5′-diphenyl-9-ethyl-3,3′-disulfopropyloxacarbocyanine

*15 7-Chloro-6-methyl-2-[1-{2-octyloxy-5-(2-octyloxy-t-octylbenzenesulfonamido)-2-propyl]-1H-pyrazolo[1,5-b][1,2,4]triazole

*16 3,3,3′,3′-Tetramethyl-5,6,5′,6′-tetrapropoxy-1,1′-bisspiroindane

*17 3-(2-Ethylhexyloxycarbonyloxy)-1-(3-hexadecyloxyphenyl)-2-pyrazoline

*18 2-Methyl-5-t-octylhydroquinone

*19 Trioctyl phosphate

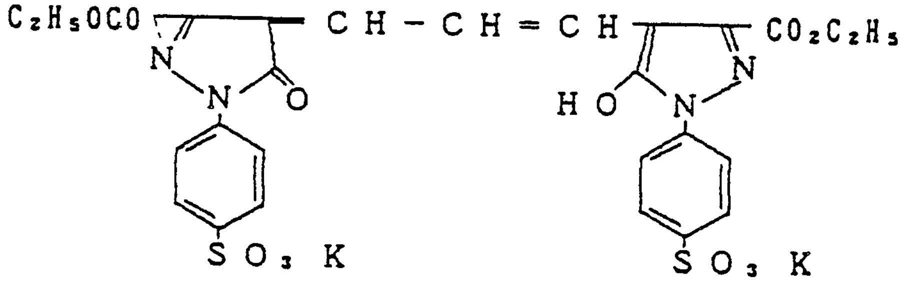
*20 Triethylammonium 3-[2-(3-benzylrhodanine-5-indene)-3-benzoxazolinyl]propanesulfonate

*21 α-Pivaloyl-α-[(2,4-dioxo-1-benzyl-5-ethoxyhydantoin-3-yl)-2-chloro-5-(α-2,4-di-t-amylphenoxy)-butanamido]acetanilide

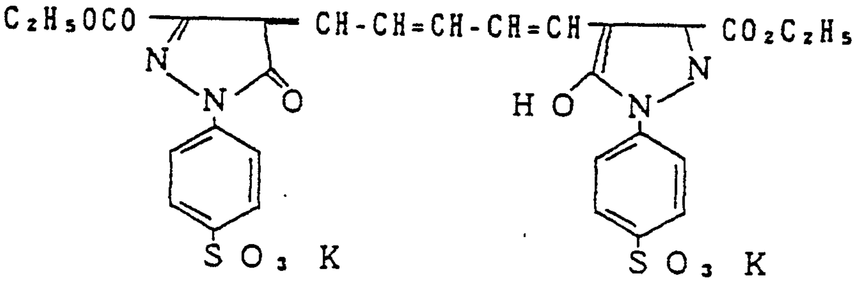
*22 5-Chloro-2-(2-hydroxy-3-t-butyl-5-t-octyl)phenylbenzotriazole

*23 2,5-Di-sec-octylhydroquinone

*24



*25



*26 1,2-Bis(vinylsulfonylacetamido)ethane

Samples 12 to 18 were prepared in the same manner as in the preparation of Sample 11 except that the compounds of the present invention were added.

A Macbeth color checker was photographed using a coupler incorporated color reversal film RDP (a product of Fuji Photo Film Co., Ltd.) and the film was processed with CR-56P to obtain a color positive film which was then used as the color positive original. The original was printed on the color reversal paper of Samples 11 to 18 using subtractive color photography. Printing was adjusted using a YMC filter so that the gray color of neutral 5 of a Macbeth color checker became a gray color having a density of 1.0 on the print. Development was carried out in the stages described below. The HVC values of the Munsell notation were measured to examine the red, green and blue color reproducibility of the resulting image. The resulting C values are shown in Table 2 below.

In order to examine the degree of stain of the image of each sample, the stain being caused by dye remaining after processing, Samples 11 to 18 were exposed through plain glass by using a sensitometer (500 CMS, color temperature: 3,200° K) and processed. The cyan density of each of the resulting samples was measured using a Macbeth densitometer.

The samples were processed with the following processing solutions in the following processing stages using an automatic processor until the accumulated replenishment rate of the processing solutions reached three times the tank capacity.

Processing Stage	Time	Temperature	Tank Solution Capacity	Replenishment Rate
	(sec)	(°C)	(liter)	(ml/m^2)
First Development	75	38	8	300
First Rinsing (1)	45	33	5	--
First Rinsing (2)	45	33	5	5,000
Reversal Exposure	15	100 lux		
Color Development	135	38	15	330
Second Rinsing	45	33	5	1,000
Bleaching-Fixing (1)	60	38	7	--
Bleaching-Fixing (2)	60	38	7	220
Third Rinsing (1)	45	33	5	--
Third Rinsing (2)	45	33	5	--
Third Rinsing (3)	45	33	5	5,000
Drying	45	75		

The first rinsing stage and the third rinsing stage were a countercurrent rinsing system such that rinsing water was allowed to flow into the first rinsing (2), overflow solution therefrom was fed to the first rinsing (1), rinsing water was allowed to flow into the third rinsing (3), overflow solution therefrom was fed to the third rinsing (2) and overflow solution from the third rinsing (2) was fed to the third rinsing (1).

Each processing solution had the following composition.

First Development:	Tank Solution	Replenisher
Pentasodium Salt of Nitrilo-N,N,N-trimethylenephosphonic Acid	1.0 g	1.0 g
Pentasodium Diethylenetriaminepentaacetate	3.0 g	3.0 g
Potassium Sulfite	30.0 g	30.0 g
Potassium Thiocyanate	1.2 g	1.2 g
Potassium Carbonate	35.0 g	35.0 g
Potassium Hydroquinonemonosulfonate	25.0 g	25.0 g
1-Phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidone	2.0 g	2.0 g
Potassium Bromide	0.5 g	--
Potassium Iodide	5.0 mg	--
Water to make	1,000 ml	1,000 ml
pH	9.60	9.70

The pH was adjusted with hydrochloric acid or potassium hydroxide.

Color Development:		
	Tank Solution	Replenisher
Benzyl Alcohol	15.0 ml	18.0 ml
Diethylene Glycol	12.0 ml	14.0 ml
3,6-Dithia-1,8-octanediol	0.20 g	0.25 g
Pentasodium Salt of Nitrilo-N,N,N-trimethylenephosphonic Acid	0.5 g	0.5 g
Pentasodium Diethylenetriaminepentaacetic Acid	2.0 g	2.0 g
Sodium Sulfite	2.0 g	2.5 g
Hydroxylamine Sulfate	3.0 g	3.6 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methylaminoaniline Sulfate	5.0 g	8.0 g
Fluorescent Brightener (diaminostilbene type)	1.0 g	1.2 g
Potassium Bromide	0.5 g	--
Potassium Iodide	1.0 mg	--
Water to make	1,000 ml	1,000 ml
pH	10.25	10.40
The pH was adjusted with hydrochloric acid or potassium hydroxide.		

Bleaching-Fixing Solution (tank solution and replenisher being the same)	
Disodium Ethylenediaminetetraacetate Dihydrate	5.0 g
Ethylenediaminetetraacetic Acid Fe(III) Ammonium Monohydrate	80.0 g
Sodium Sulfite	15.0 g
Ammonium Thiosulfate (700 g/liter)	160 ml
2-Mercapto-1,3,4-triazole	0.5 g
Water to make	1,000 ml
pH	6.50
The pH was adjusted with acetic acid or aqueous ammonia.	

These results together with the dyes (amounts thereof and layers to which dyes were added) are shown in Table 2 below.

TABLE 2

Sample No.	Dye Additionally Added to 11th Layer	Amount Added	Maximum Wavelength in Gelatin Film	Half Width	Color Reproducibility (C Value)			Stain after Processing (C Density)	Remarks
		(g/m^2)	(nm)	(nm)	Red	Green	Blue		
11	None	--	--	--	10.2	8.0	6.3	0.14	Comparison
12	I-2	0.02	620	75	11.2	8.8	6.3	0.14	Invention
13	II-2	0.02	624	45	11.3	8.7	6.3	0.14	Invention
14	III-12	0.02	525	60	10.4	8.5	6.9	0.14	Invention
15	IV-2	0.02	514	58	10.6	8.4	6.8	0.14	Invention
16	I-2	0.01	620	75	11.2	8.9	6.9	0.14	Invention
	IV-2	0.01	514	58					
17	III-12	0.02	525	60	11.1	9.2	6.8	0.14	Invention
	II-2	0.02	624	45					
18	IV-2	0.01	514	58	11.3	9.3	6.7	0.14	Invention
	IV-9	0.01	615	62					

It is clear from Table 2 that Samples 12 to 18 of the present invention gave prints having excellent color reproducibility without staining after processing occurring.

EXAMPLE 3

Sample 19 was prepared in the same way as in Example 1 except that the compositions of the sensitive layers were modified in the following manner.

1. Eleventh Layer:	Yellow Coupler (Y-35)	0.35 g/m^2
2. Twelfth Layer:	Yellow Coupler (Y-35)	0.30 g/m^2
3. Thirteenth Layer:	Irradiation Preventing Dye (Cpd-18, Cpd-19, Cpd-20, Cpd-21 in a weight ratio of 10/10/14/16)	0.05 g/m^2
4. Fifteenth Layer:	Dye was not present.	

Each sample was subjected to a running test in the same manner as in Example 1 using the same processing solutions and stages as those in Example 1.

Samples 20 to 27 were prepared in the same manner as in the preparation of Sample 19 except that the compounds of the present invention and comparative compounds were used in combination with or in place of the irradiation preventing dye of the Thirteenth Layer of Sample 19. The structures of Samples 19 to 27 are shown in Table 3 below.

The samples were tested in the same manner as in Example 1 to evaluate color reproducibility.

The resulting C values are shown in Table 3 below. A higher C value means that the color of the sample is reproduced with higher chroma. It was confirmed that large and small values corresponded to the brightness of each color when prints were visually examined.

Samples 19 to 27 were exposed through an optical wedge using white light of 3,200 °K. The exposed samples were processed in the manner described above. The relative sensitivity at an optical density of 1.0 and maximum density (Dmax) were measured.

Further, Samples 19 to 27 were stored at 50 °C and RH of 80% for 3 days. Samples 19 to 27 were stored in a refrigerator at 0 °C for the same period of time. These samples were exposed and developed in the same manner as those described above. The relative sensitivity of each sample (stored at 50 °C and RH of 80%) to the sensitivity of each sample (stored in the refrigerator) was determined.

The results are shown as preservability in Table 3 below.

TABLE 3

Sample No.	Dye (g/m^2)	Yellow Coupler	Preservability (change in relative sensitivity)	Dmax	Color Reproducibility (C value) Red	Color Reproducibility (C value) Green	Color Reproducibility (C value) Blue
19 (Comparison)	Cpd-18 0.010 Cpd-19 0.010 Cpd-20 0.014 Cpd-21 0.016	(Y-35)	80	2.10	9.8	8.8	6.8
20 (Comparison)	"	(Y) (shown below)	75	1.82	9.7	8.5	6.7
21 (Invention)	Cpd-18 0.005 Cpd-19 0.005 Cpd-20 0.007 Cpd-21 0.008 II-2 0.015	(Y-35)	95	2.30	10.2	9.2	6.8
22 (Invention)	"	(Y-40)	96	2.35	10.3	9.3	6.9

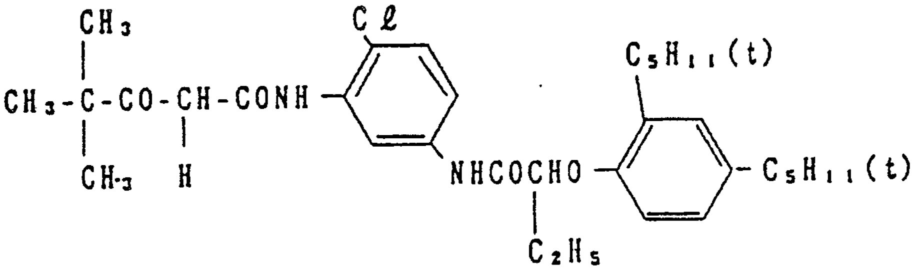
TABLE 3 (cont'd)

Sample No.	Dye	(g/m^2)	Yellow Coupler	Preservability (change in relative sensitivity)	Dmax	Color Reproducibility (C value)		
						Red	Green	Blue
23 (Comparison)	Cpd-18	0.005	(Y) (shown below)	85	1.85	10.0	9.0	6.8
	Cpd-19	0.005						
	Cpd-20	0.007						
	Cpd-21	0.008						
	II-2	0.015						
24 (Invention)	Cpd-18	0.010	(Y-35)	80	2.33	10.5	9.3	6.9
	Cpd-19	0.010						
	Cpd-20	0.014						
	Cpd-21	0.016						
	II-2	0.015						

TABLE 3 (cont'd)

Sample No.	Dye (g/m^2)		Yellow Coupler	Preservability (change in relative sensitivity)	Dmax	Color Reproducibility (C value) Red	Green	Blue
25 (Invention)	Cpd-18	0.005	(Y-35)	98	2.28	10.7	9.5	6.9
	Cpd-19	0.005						
	Cpd-20	0.007						
	Cpd-21	0.008						
	II-12	0.015						
26 (Invention)	Cpd-18	0.005	(Y-35)	98	2.39	10.6	9.2	6.8
	Cpd-19	0.005						
	Cpd-20	0.007						
	Cpd-21	0.008						
	II-13	0.015						
27 (Invention)	II-2	0.05	(Y-35)	99	2.32	10.9	9.5	6.9

(Y) Comparative Yellow Coupler



It is apparent from the results in Table 3 that the samples of the present invention have high Dmax values and scarcely cause deterioration (reduction in sensitivity) during photographic material storage conditions as compared with the comparative samples. Further, the samples of the present invention show high C values and have excellent color reproducibility as compared with the comparative samples.

EXAMPLE 4

Sample 28 was prepared in the same manner as in Example 1 except that C-2, C-9 (a ratio of 1/1) as cyan couplers in an amount of 0.30 g/m^2 were used for the Third and Fourth Layers, Cpd-18, Cpd-19, Cpd-20, Cpd-21 (a ratio of 10/10/14/16) as irradiation preventing dyes in an amount of 0.05 g/m^2 were used for the Thirteenth Layer and Fifteenth Layer contained no dye.

Each sample was subjected to a running test in the same manner as in Example 1 using the same processing stages and processing solutions as those in Example 1.

Samples 29 to 36 were prepared in the same manner as in the preparation of Sample 28 except that the compounds of the present invention and the comparative compounds were used in combination with or in place of the irradiation preventing dye of the Thirteenth Layer of Sample 28.

The structures of Samples 28 to 36 are shown in Table 4 below. The samples were tested in the same manner as in Example 1 to evaluate color reproducibility.

The resulting C values are shown in Table 4 below. A higher C value means that the color of the sample is reproduced with higher chroma. It was confirmed that large and small values corresponded to the brightness of each color when prints were visually examined.

Samples 28 to 36 were exposed (1/10 sec) with white light of 3,200 °K (500 CMS) and processed in the same manner described above. The cyan density of each sample was measured. The results are shown as fog value in Table 4 below.

The C.T.F. (%) at a space frequency of 15/mm was determined. The results obtained are shown in Table 4 below.

TABLE 4

Sample No.	Dye (g/m^2)	Cyan Coupler	Fog Value (R)	Sharpness (R)	Color Reproducibility (C value) Red	Color Reproducibility (C value) Green	Color Reproducibility (C value) Blue
28 (Comparison)	Cpd-18 0.010 Cpd-19 0.010 Cpd-20 0.014 Cpd-21 0.016	C- 2 C- 9	0.14	30.0	9.6	8.7	6.8
29 (Comparison)	"	C- 3	0.15	28.8	9.8	8.6	6.8
30 (Invention)	Cpd-18 0.005 Cpd-19 0.005 Cpd-20 0.007 Cpd-21 0.008 II-2 0.015	C- 2 C- 9	0.12	32.2	10.2	9.5	6.9
31 (Invention)	"	C- 3	0.12	32.0	10.5	9.7	7.1
32 (Invention)	"	C-18	0.13	33.1	10.1	9.5	6.8

TABLE 4 (cont'd)

Sample No.	Dye (g/m^2)		Cyan Coupler	Fog Value (R)	Sharpness (R)	Color Reproducibility (C value)		
						Red	Green	Blue
33 (Invention)	Cpd-18	0.010	C- 2 C- 9	0.11	32.8	10.3	9.6	6.9
	Cpd-19	0.010						
	Cpd-20	0.014						
	Cpd-21	0.016						
	II-2	0.015						
34 (Invention)	Cpd-18	0.005	"	0.12	31.5	10.5	9.6	7.0
	Cpd-19	0.005						
	Cpd-20	0.007						
	Cpd-21	0.008						
	II-12	0.015						

TABLE 4 (cont'd)

Sample No.	Dye (g/m²)		Cyan Coupler	Fog Value (R)	Sharpness (R)	Color Reproducibility (C value)		
						Red	Green	Blue
35 (Invention)	Cpd-18	0.005	C- 2	0.11	32.0	10.5	9.8	6.8
	Cpd-19	0.005	C- 9					
	Cpd-20	0.007						
	Cpd-21	0.008						
	II-13	0.015						
36 (Invention)	II-2	0.65	"	0.12	33.8	10.9	9.9	7.3

It is apparent from the results in Table 4 that the samples containing the cyan couplers and dyes of the present invention are photographic materials which have low fogged and have excellent color reproducibility and sharpness.

Example 5

Sample 37 was prepared in the same manner as in Example 1 except that the Thirteenth Layer contained no irradiation preventing dye and the Fifteenth Layer contained no dye.

This sample was subjected to a running test in the same manner as in Example 1 using the same processing stages and processing solutions as those in Example 1.

Samples 38 to 46 were prepared in the same manner as in the preparation of Sample 37 except that the dyes of the present invention and comparative compound were added to the Thirteenth Layer, these dyes and comparative compound being shown in Table 5 below. These samples were processed in the same manner as in Sample 37.

These samples were tested in the same manner as in Example 1 to evaluate color reproducibility. The HVC values were measured.

The resulting C values are shown in Table 5 below. A higher C value means that the color of the sample is reproduced with higher saturation. It was confirmed that large and small values corresponded to the brightness of each color when the prints are visually examined.

Further, the degree of stain of the image on the color print after processing was examined, this stain being caused by the dye remaining after processing. Samples 37 to 46 were exposed (1/10 sec) to white light of 3,200°K (500 CMS), and processed in the same manner as that described above. Of the development stages, the color forming stage was reduced from 135 seconds (standard) to 30 seconds to intensify the degree of stain. The color formation of the dye image due to the coupler scarcely occurred under the above condition and hence a difference in density between the resulting samples was considered as a difference in the amount of the dye left behind. The C.T.F. (%) at a space frequency of 15/mm was determined. The results obtained are shown in Table 5 below. A larger C.T.F. value means that the photographic material had better sharpness.

TABLE 5

Sample No.	Dye Added to 13th Layer (g/m²)	Density of Stain due to Dye Left Behind			Sharpness (CTF %)			Color Reproducibility (C value)		
		B	G	R	Red-Sensitive Layer	Green-Sensitive Layer	Blue-Sensitive Layer	Red	Green	Blue
37 (Comparison)	None	0.123	0.146	0.140	27.5	27.8	26.5	9.4	7.5	6.5
38 (Comparison)	II-2 (0.05)	0.128	0.151	0.143	29.5	29.3	29.0	9.9	7.9	6.6
39 (Comparison)	I-60 (0.05)	0.125	0.150	0.141	27.8	33.8	30.5	9.4	7.6	6.5
40 (Comparison)	I-2 (0.05)	0.125	0.155	0.148	28.3	29.2	31.2	10.2	8.1	6.7
41 (Comparison)	I-39 (0.025) I-60 (0.025)	0.125	0.150	0.142	30.5	31.2	30.6	9.4	7.6	6.5
42 (Comparison)	I-56 (0.05)	0.124	0.150	0.141	31.2	33.5	31.5	9.5	7.5	6.6
43 (Invention)	II-2 (0.03) I-32 (0.02)	0.123	0.147	0.141	34.8	34.2	33.0	10.4	8.6	6.7
44 (Invention)	II-2 (0.03) I-39 (0.02)	0.123	0.149	0.144	34.6	34.5	33.1	10.8	8.9	6.8
45 (Invention)	II-2 (0.03) I-59 (0.02)	0.123	0.147	0.141	33.5	33.9	33.0	10.9	9.1	6.9

TABLE 5 (cont'd)

Sample No.	Dye Added to 13th Layer (g/m^2)	Density of Stain due to Dye Left Behind			Sharpness (CTF %)			Color Reproducibility (C value)		
		B	G	R	Red-Sensitive Layer	Green-Sensitive Layer	Blue-Sensitive Layer	Red	Green	Blue
46 (Invention)	II-2 (0.02) I-39 (0.02) I-60 (0.02)	0.124	0.148	0.143	36.0	34.6	33.3	10.7	9.1	6.8

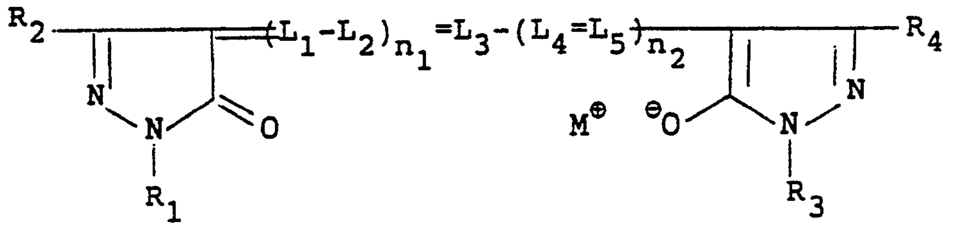
It is apparent from the results in Table 5 above that when the dyes of the present invention are used in combination with Compound II-2, a color is not formed by the dye remaining and a photographic material having improved sharpness as well as color reproducibility can be obtained. However, when Compound II-2 alone is used, it is impossible for coloration after processing to be prevented and further sharpness as well as color reproducibility are improved.

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

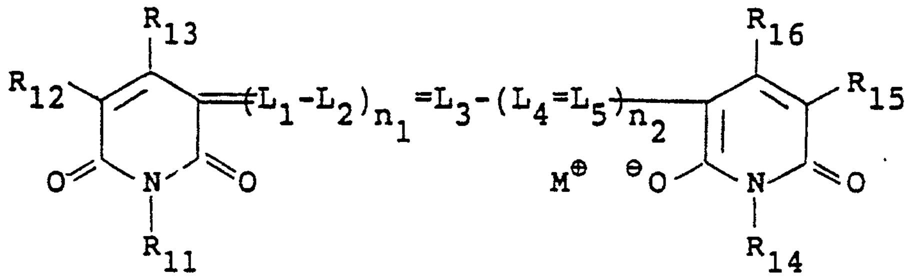
1. A positive working silver halide color photographic material comprising a support having thereon at least one silver halide emulsion layer, wherein the photographic material contains (a) at least one dye having a maximum absorption wavelength of 480 to 530 nm in a gelatin film and/or (b) at least one dye having a maximum absorption wavelength of 580 to 630 nm in a gelatin film with the proviso that an oxonol dye having a hydroxypyridone nucleus is excluded when a dye (a) or a dye (b) is used alone.

2. A positive working silver halide color photographic material as in Claim 1, wherein said dye is a compound represented by the following general formula (I), (II), (III) or (IV):



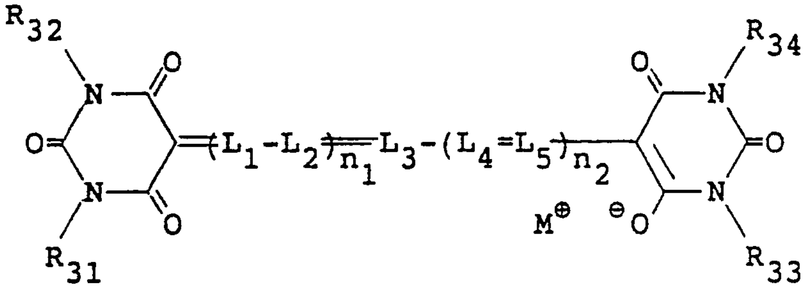
(I)

wherein R_1 and R_3, which may be the same or different, each represents an aliphatic group, an aromatic group or a heterocyclic ring; R_2 and R_4, which may be the same or different, each represents an aliphatic group, an aromatic group, $-OR_5$, $-COOR_5$, $-NR_5R_6$, $-CONR_5R_6$, $-NR_5CONR_5R_6$, $-SO_2R_7$, $-COR_7$, $-NR_6COR_7$, $-NR_6SO_2R_7$, or a cyano group, wherein R_5 and R_6, which may be the same or different, each represents a hydrogen atom, an aliphatic group or an aromatic group; R_7 represents an aliphatic group or an aromatic group; R_5 and R_6 or R_6 and R_7 may combine to form a 5-membered or 6-membered ring; n_1 and n_2 each represents 0 or 1; $M^{\oplus}$ represents a hydrogen atom or a monovalent cation; L_1, L_2, L_3, L_4 and L_5 each represents a methine group;

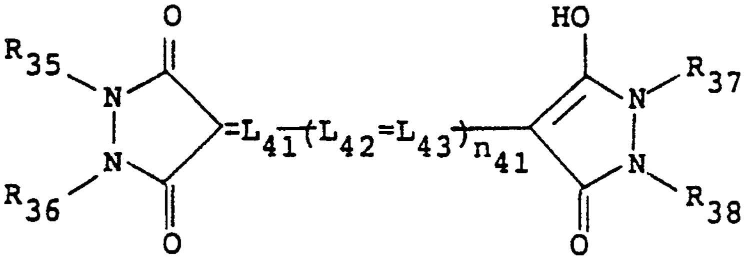


(II)

wherein R_{11} and R_{14}, which may be the same or different, each represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, $-NR_{17}R_{18}$, $-NR_{17}CONR_{17}R_{18}$, $-NR_{18}COR_{19}$, or $-NR_{18}SO_2R_{19}$; R_{12} and R_{15}, which may be the same or different, each represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a sulfo group, $-NR_{17}R_{18}$, $-NR_{18}COR_{19}$, $-NR_{18}SO_2R_{19}$, $-NR_{17}CONR_{17}R_{18}$, $-COOR_{17}$, $-CONR_{17}R_{18}$, $-COR_{19}$, $-SO_2R_{19}$ or $-SO_2NR_{17}R_{18}$; R_{13} and R_{16}, which may be the same or different, each represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, $-OR_{17}$, $-COOR_{17}$, $-COR_{19}$, $-CONR_{17}R_{18}$, $-NR_{17}R_{18}$, $-NR_{18}COR_{19}$ or $-NR_{18}SO_2R_{19}$, $-NR_{17}COR_{17}R_{18}$, $-SO_2R_{19}$, $-SO_2NR_{17}R_{18}$, $-OR_7$ or a cyano group; R_{17} and R_{18}, which may be the same or different, each represents a hydrogen atom, an aliphatic group or an aromatic group; R_{19} represents an aliphatic group or an aromatic group; R_{17} and R_{18} or R_{18} and R_{19} may combine to form a 5-membered or 6-membered ring; and L_1, L_2, L_3, L_4, L_5, n_1, n_2 and $M^{\oplus}$ are as defined above in the formula (I);


(III)

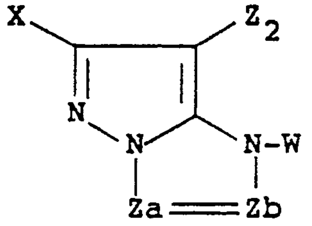
wherein R_{31}, R_{32}, R_{33} and R_{34}, which may be the same or different, each represents a hydrogen atom, an aliphatic group, an aromatic group or a heterocyclic group; and L_1 L_2, L_3, L_4, L_5, n_1, n_2 and $M^{\oplus}$ are as defined in the formula (I);


(IV)

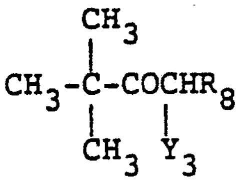
wherein R_{35}, R_{36}, R_{37} and R_{38}, which may be the same or different, each represents an aliphatic group, an aromatic group or a heterocyclic group; L_{41}, L_{42} and L_{43} each represents a machine group; n_{41} represents 1, 2 or 3; and one or more of R_{35}, R_{36}, R_{37} and R_{38} are a carboxyl group or a sulfo group and the total of the carboxyl groups and/or the sulfo groups is at least two.

3. A positive working silver halide color photographic material as in Claim 2, wherein R_2 and R_4 in formula (I) each represents $-OR_5$ or $-NR_5R_6$, in which R_5 and R_6 are the same as defined in formula (I).

4. A positive working silver halide color photographic material as in Claim 1, wherein said photographic material contains at least one magenta coupler represented by the following formula (V), at least one yellow coupler represented by the following formula (VI) and at least one cyan coupler represented by the following formula (VII) or (VIII):

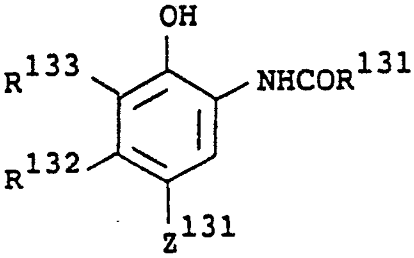

(V)

wherein X represents a hydrogen atom or a substituent group; Z_2 represents a hydrogen atom or a group which is eliminated by coupling with the oxidation product of an aromatic primary amine developing agent; W represents a hydrogen atom, an acyl group, an aliphatic sulfonyl group or an aromatic sulfonyl group; Za and Zb each represents a methine group, a substituted methine group or -N=; and a dimer or polymer may be formed by X, Za or a substituted methine group of Za or Zb;



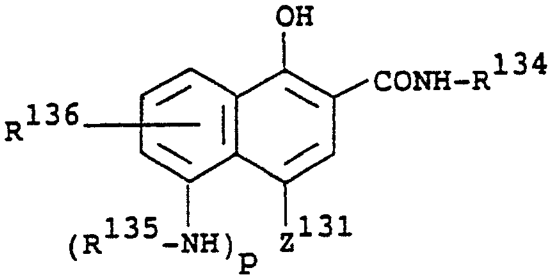
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CO\underset{Y_3}{CH}R_8 \qquad (VI)$$

wherein R_8 represents a substituted or unsubstituted N-phenylcarbamoyl group; Y_3 represents a group which is bonded through an oxygen atom or a nitrogen atom and is eliminated by coupling with the oxidation product of an aromatic primary amine color developing agent;



(VII)

wherein R^{131} represents an alkyl group, an aryl group, an amino group or a heterocyclic group; R^{132} represents an acylamino group or an alkyl group; R^{133} represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; R^{133} and R^{132} may combine together to form a 5 membered to 7-membered ring; and Z^{131} represents a hydrogen atom, a halogen atom or a group which is eliminated by reaction with the oxidation product of an aromatic primary amine color developing agent;



(VIII)

wherein R^{134} represents an alkyl group, an aryl group or a heterocyclic group; R^{135} represents an acyl group, a sulfonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group or an alkoxysulfonyl group; R^{136} repre sents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an aryloxy group, an amido group, an imido group, an alkylthio group, an arylthio group, a ureido group, an alkylsulfonyl group or an arylsulfonyl group; p represents 0 or 1; and Z^{131} represents a hydrogen atom or a group which is eliminated by reaction with the oxidation product of an aromatic primary amine color developing agent.