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(54) Silver halide color photographic material.

(57) A silver halide color photogtaphic material is disclosed, comprising a support having provided thereon at least one silver halide emulsion layer containing a cyan coupler, at least one silver halide emulsion layer containing a magenta coupler, and at least one silver halide emulsion layer containing a yellow coupler, in which said cyan coupler-containing emulsion layer contains (l) at least one of a specified type of cyan coupler, and (2) a high-boiling organic solvent in an amount of not more than 30% by weight based on the total amount of said specified type of cyan coupler. The photographic material exhibits improved sharpness without being accompanied by reduction in color developability or precipitation of crystals. These effects can be enhanced by using 2-equivalent polymeric magenta couplers in combination.

SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

This invention relates to a silver halide color photographic material, and more particularly to a silver halide color photographic material which forms a cyan dye image whose density is not reduced even when processed with a bleaching bath or bleach-fix bath has been fatiqued or otherwise has a weak oxidizing capacity, and also forms an image excellent in sharpness.

BACKGROUND OF THE INVENTION

It is well known that an aromatic primary amine color developing agent oxidized with an exposed silver halide can be reacted with a coupler to produce a dye, such as indophenol dyes, indoaniline dyes, indamine dyes, azomethine dyes, phenoxazine dyes, phenadine dyes, or the like, to form a dye image.

Of such couplers, phenolic couplers or naphthoic couplers known as cyan dye image forming couplers have been noted to have a disadvantage that the dye image produced therefrom has low fastness to heat or light, or undergoes density reduction when processed with a bleaching bath or bleach-fix bath having weak oxidizing capacity or a fatigued bleaching bath or bleach-fix bath. In order to overcome this disadvantage, phenolic cyan couplers having a phenylureido group at the 2-position and a carbonamido group at the 5-position have been disclosed, e.g., in Japanese Patent Application (OPI) Nos. 33249/83 and 33250/73 (the term "OPI" as used herein means "unexamined published application") and U.S. Patent 4,444,872. Although such cyan couplers are superior in the above-described respects to conventional phenolic or naphthoic cyan couplers, they involve disadvantages in that the spectral absorption of the dye image produced is liable to great variation depending on the density, in that a precipitate would be formed or color developability would be reduced due to poor solubility unless a sufficient amount of a high-boiling organic solvent is used, and the like, as has pointed out in U.S. Patent 4,594,314. Therefore, use of these phenolic couplers inevitably increases the film thickness, resulting in deterioration of image sharpness.

In an attempt to decrease color density dependence of the spectral absorption of the above-described couplers, naphthoic cyan couplers having an amido group at the 5-position have been described in European Patent 161626A. However, the objects and effects of the present invention are not described in European Patent 161626A.

Japanese Patent Application (OPI) No. 11452/81 discloses a light-sensitive material containing a high-boiling point organic solvent in an amount of from 0.01 to 0.3% by weight based on a total amount of 5-pyrazolone magenta couplers. However, this technique aims at improvement on resistance to formaldehyde, and is, hence, entirely different from the present invention, from the standpoint of developed hue and effects.

SUMMARY OF THE INVENTION

One object of this invention is to provide a silver halide color photographic light-sensitive material which does not undergo reduction in cyan color density even when processed with a bleaching bath or bleach-fix bath having been fatigued or having a weak oxidizing capacity.

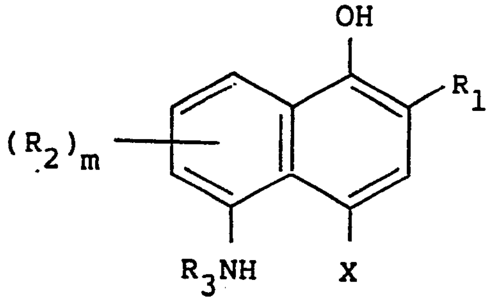
Another object of this invention is to provide a silver halide color photographic light-sensitive material having excellent dye image preservability.

A further object of this invention is to provide a silver halide color photographic material having excellent sharpness.

As a result of extensive investigations, the present inventors have found that combined use of these couplers with a small amount of a high-boiling point organic solvent is freed from deterioration of color developability or precipitation as encountered with the combined use of phenolic couplers having a ureido group at the 2-position and a small amount of a high-boiling organic solvent, while retaining the superiority of such phenolic couplers. It has also been found that application of such a coupler-solvent combination to light-sensitive materials containing 2-equivalent polymeric magenta couplers as magenta couplers produces a further pronounced effect.

It has now been found that the above objects can be accomplished by a silver halide color photographic material comprising a support having provided thereon at least one silver halide emulsion layer containing a cyan coupler, at least one silver halide emulsion layer containing a magenta coupler, and at least one silver halide emulsion layer containing a yellow coupler, wherein said cyan coupler-containing emulsion layer contains at least one cyan coupler represented by formula (I) shown below and a high-boiling point organic solvent in an amount of not more than 30% by weight based on the total amount of said cyan coupler(s).

Formula (I) is represented by



(I)

wherein R_1 represents $-CONR_5R_6$, $-NHCOR_5$, $-NHCOOR_7$, $-NHSO_2R_7$, $-NHCONR_5R_6$ or $-NHSO_2NR_5R_6$, wherein R_5 and R_6 (which may be the same or different) each represents a hydrogen atom, an aliphatic group, an aromatic group or a heterocyclic group, or R_5 and R_6 are taken together to form a nitrogen-containing heterocyclic ring, and R_7 represents an aliphatic group, an aromatic group or a heterocyclic group; R_2 represents a group capable of substituting for a hydrogen atom of a naphthalene ring, or a plurality of R_2 - (which may be the same or different) groups together form a ring; m represents 0 or an integer of from 1 to 3; R_3 represents a monovalent organic group; and X represents a hydrogen atom or a group releasable upon coupling with an oxidation product of an aromatic primary amine developing agent, or R_3 together with R_2 or X form a ring.

DETAILED DESCRIPTION OF THE INVENTION

In formula (I), R_6 and R_7 in groups represent ing R_1 each preferably represents an aliphatic group having from 1 to 30 carbon atoms, an aromatic group having from 6 to 30 carbon atoms, and a heterocyclic group having from 2 to 30 carbon atoms.

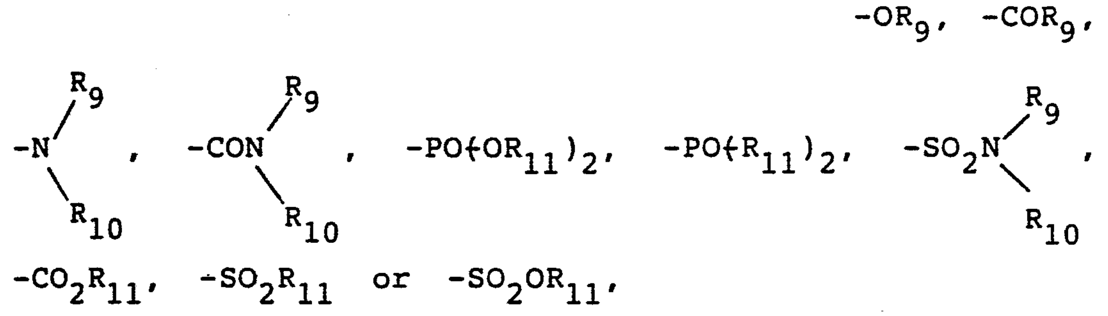
Typical examples of the group (or atom, hereinafter the same) capable of substituting for a hydrogen atom of a naphthalene ring as represented by R_2 include a halogen atom, a hydroxyl group, an amino group, a carboxyl group, a sulfonic acid group, a cyano group, an aliphatic group, an aromatic group, a heterocyclic group, a carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a ureido group, an acyl group, an acyloxy group, an aliphatic oxy group, an aromatic oxy group, an aliphatic thio group, an aromatic thio group, an aliphatic sulfonyl group, an aromatic sulfonyl group, a sulfamoylamino group, a nitro group, an imido group, etc. These groups for R_2 contain up to 30 carbon atoms in total. When m is 2, $(R_2)_m$ represents, for example, a dioxymethylene group.

The monovalent organic group as represented by R_3 preferably includes a group represented by formula (II)

$R_8(Y)_n$-   (II)

wherein Y represents $>NH$, $>CO$ or $>SO_2$;

n represents 0 or 1; and R_8 represents a hydrogen atom, an aliphatic group having from 1 to 30 carbon atoms, an aromatic group having from 6 to 30 carbon atoms, a heterocyclic group having from 2 to 30 carbon atoms,



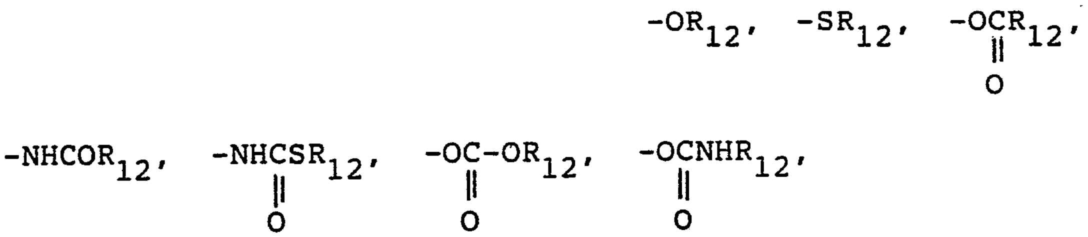
$$-OR_9,\ -COR_9,\ -N\begin{matrix}R_9\\ R_{10}\end{matrix},\ -CON\begin{matrix}R_9\\ R_{10}\end{matrix},\ -PO(OR_{11})_2,\ -PO(R_{11})_2,\ -SO_2N\begin{matrix}R_9\\ R_{10}\end{matrix},$$

$$-CO_2R_{11},\ -SO_2R_{11}\ \text{or}\ -SO_2OR_{11},$$

wherein R_9, R_{10}, and R_{11} each has the same meaning as R_5, R_6, and R_7 as above defined, and R_9 and R_{10} may be taken together to form a nitrogen-containing heterocyclic ring.

Examples of the nitrogen-containing heterocyclic ring formed by $-NR_5R_6$ or $-NR_9R_{10}$ include a morpholine ring, a piperidine ring, a pyrrolidine ring, etc.

Typical examples of the group (or atom, hereinafter the same) releasable upon coupling as represented by X include a halogen atom,



$$-OR_{12},\ -SR_{12},\ -O\overset{\displaystyle O}{\underset{}{C}}R_{12},$$

$$-NHCOR_{12},\ -NH\underset{\displaystyle O}{\underset{\|}{C}}SR_{12},\ -O\underset{\displaystyle O}{\underset{\|}{C}}-OR_{12},\ -O\underset{\displaystyle O}{\underset{\|}{C}}NHR_{12},$$

an aromatic azo group having from 6 to 30 carbon atoms, a heterocyclic group having from 1 to 30 carbon atoms containing a nitrogen atom at which to bond to the coupling position of the coupler (e.g., succinimido group, a phthalimido group, a hydantoinyl group a pyrazolyl group, a 2-benzotriazolyl group, etc.), etc., wherein R_{12} represents an aliphatic group having from 1 to 30 carbon atoms, an aromatic group having from 6 to 30 carbon atoms or a heterocyclic group having from 2 to 30 carbon atoms.

The expression "aliphatic group" as used herein includes saturated or unsaturated, substituted or unsubstituted, and straight or branched chain or cyclic groups. Typical examples of the aliphatic group are a methyl group, an ethyl group, a butyl group, a cyclohexyl group, an allyl group, a propargyl group, a methoxyethyl group, an n-decyl group, an n-dodecyl group, an n-hexadecyl group, a trifluoromethyl group, a heptafluoropropyl group, a dodecyloxypropyl group, a 2,4-di-t-amylphenoxypropyl group, a 2,4-di-t-amylphenoxybutyl group, etc.

The expression "aromatic group" as used herein includes substituted or unsubstituted groups. Typical examples of the aromatic group are a phenyl group, a tolyl group, a 2-tetradecyloxyphenyl group, a pentafluorophenyl group, a 2-chloro-5-dodecyloxycarbonylphenyl group, a 4-chlorophenyl group, a 4-cyanophenyl group, a 4-hydroxyphenyl group, etc.

The expression "heterocyclic group" as used herein includes substituted or unsubstituted groups. Typical examples of the heterocyclic groups are a 2-pyridyl group, a 4-pyridyl group, a 2-furyl group, a 4-thienyl group, a quinolinyl group, etc.

In formula (I), R_1 preferably represents $-CONR_5R_6$. Specific examples of $-CONR_5R_6$ include a carbamoyl group, an ethylcarbamoyl group, a morpholinocarbonyl group, a dodecylcarbamoyl group, a hexadecylcarbamoyl group, a decyloxypropylcarbamoyl group, a dodecyloxypropylcarbamoyl group, a 2,4-di-t-amylphenoxypropylcarbamoyl group, a 2,4-di-t-amylphenoxybutylcarbamoyl group, etc.

R_2 preferably represents a halogen atom, an aliphatic group, a carbonamido group, a sulfonamido group, etc. More preferably m in $(R)_m$ is zero.

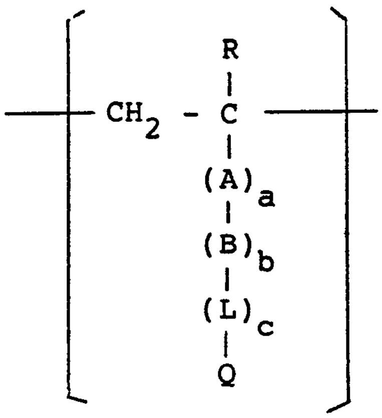
R_3 preferably represents the group of formula (II) wherein n is 0, and R_8 represnets $-COR_9$ (e.g., a formyl group, an acetyl group, a trifluoroacetyl group, a chloroacetyl group, a benzoyl group, a pentafluorobenzoyl group, a p-chlorobenzoyl group, etc.), $-COOR_{11}$ (e.g., a methoxycarbonyl group, an ethoxycarbonyl group, a butoxycarbonyl group, a decyloxycarbonyl group, a methoxyethoxycarbonyl group, a phenoxycarbonyl group, etc.), $-SO_2R_{11}$ (e.g., a methane sulfonyl group, an ethanesulfonyl group, a butanesulfonyl group, a hexadecanesulfonyl group, a benzenesulfonyl group, a toluenesulfonyl group, a p-chlorobenzenesulfonyl group, etc.), -CONR$_9$R$_{10}$ (e.g., an N,N-dimethylcarbamoyl group, an N,N-diethylcarbamoyl group, an N,N-dibutylcarbamoyl group, a morpholinocarbonyl group, a piperidinocarbonyl group, a 4-cyanophenylcarbonyl group, a 3,4-dichlorophenylcarbamoyl group, a 4-methanesulfonylphenylcarbamoyl group, etc.), -SO$_2$NR$_9$R$_{10}$ (e.g., an N,N-dimethylsulfamoyl group, an N,N-diethylsulfamoyl group, an N,N-dipropylsulfamoyl group, etc.), etc. R$_3$ more preferably represents -COOR$_{11}$, -COR$_9$ or -SO$_2$R$_{11}$ with -COOR$_{11}$ being most preferred.

X preferably represents a hydrogen atom, a chlorine atom, an aliphatic oxy group (e.g., a 2-hydroxyethoxy group, a 2-chloroethoxy group, a carboxymethyloxy group, a 1-carboxyethoxy group, a 2-methanesulfonylethoxy group, a 3-carboxypropyloxy group, a 2-methoxyethoxycarbamoylmethyloxy group, a 1-carboxytridecyl group, a 2-(1-carboxytridecylthio)ethyloxy group, a 2-carboxymethylthioethyloxy group, a 2-methanesulfonamidoethyloxy group, etc.), an aromatic oxy group (e.g., a 4-acetamidophenoxy group, a 2-acetamidophenoxy group, a 4-(3-carboxypropaneamido)phenoxy group, etc.) or a carbamoyloxy group (e.g., an ethylcarbamoyl group, a phenylcarbamoyloxy group, etc.).

The cyan coupler according to the present invention includes a polymer inclusive of a dimer wherein two or more monomer units derived from the compound of formula (I) are connected at any of R$_1$, R$_2$, R$_3$, and X via a divalent or higher valent group. In this case, each of the above-illustrated substituents may have a total carbon atom number out of the range respectively recited.

In cases where the compound of formula (I) is polymerized to form a polymeric coupler, such a polymeric coupler typically includes a homo-or copolymer of an addition polymerizable ethylenically unsaturated compound having a cyan dye forming coupler residue (cyan forming monomer). Such a polymer comprises one or more repeating units represented by formula (III) shown below, and, if desired, one or more non-color-forming ethylenically unsaturated monomers as copolymerizable units.

Formula (III) is represented by



$$\left[-CH_2-\overset{R}{\underset{(A)_a-(B)_b-(L)_c-Q}{C}}- \right] \qquad (III)$$

wherein R represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms or a chlorine atom; A represents -CONH-, -COO-or a substituted or unsubstituted phenylene group; B represents a substituted or unsubstituted alkylene, phenylene or aralkylene group; L represents -CONR'-, -NR'CONR'-, -NR'COO-, -NR'CO-, -OCONR'-, -NR'-, -COO-, -OCO-, -CO-, -O-, -SO$_2$-, -NR'SO$_2$-or -SO$_2$NR', wherein R' represents a hydrogen atom or a substituted or unsubstituted alkyl or aryl group; a, b, and c each represents 0 or 1; and Q represents a cyan coupler residual group derived from the compound represented by formula (I) by removing any one of hydrogen atoms other than the hydrogen atom of the 1-positioned hydroxyl group.

The polymeric coupler preferably includes a copolymer comprising the cyan forming monomer providing the repeating unit of formula (III) and the non-color-forming ethylenically unsaturated comonomers which do not couple with an oxidation product of an aromatic primary amine developing agent. Specific examples of such comonomers are acrylic acid, α-chloroacrylic acid, α-alacrylic acid (e.g., methacrylic acid), esters or amides of these acrylic acids (e.g., acrylamide, methacrylamide, n-butylacrylamide, t-butylacrylamide, diacetonacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, iso-butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, β,β-hydroxymethacrylate, etc.), vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl laurate, etc.), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (e.g., styrene and derivatives thereof, e.g., vinyl toluene, divinylbenzene, vinylacetophenone, sulfostyrene, etc.), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers (e.g., vinyl ethyl ether, etc.), maleic esters, N-vinyl-2-pyrrolidone, N-vinylpyridine, 2-or 4-vinylpyridine, and the like.

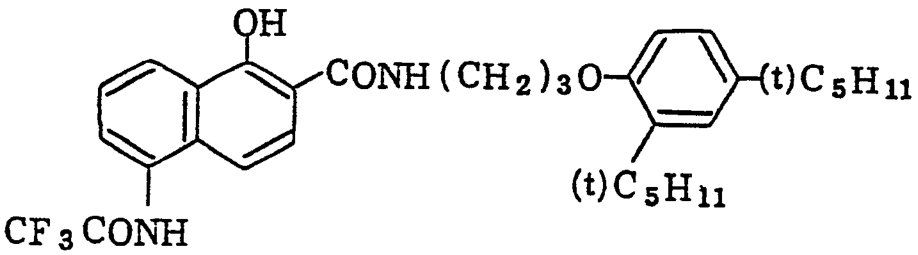
Of these comonomers, acrylic esters, methacrylic esters, and maleic esters are preferred. These non-color-forming ethylenically unsaturated monomers may be used either individually or in combinations of two or more thereof. For example, a combination of methyl acrylate and butyl acrylate, a combination of butyl acrylate and styrene, a combination of butyl methacrylate and methacrylic acid, a combination of methyl acrylate and diacetonacrylamide, etc. can be employed.

As is well known in the art of polymeric couplers, the kind of the ethylenically unsaturated monomers to be copolymerized with vinyl monomers corresponding to the repeating unit of formula (III) can be selected appropriately so as to exert favorable influences upon physical and/or chemical properties of the resulting copolymers, such as solubility, compatibility with binders for photographic colloidal compositions, e.g., gelatin, flexibility, heat stability, and the like.

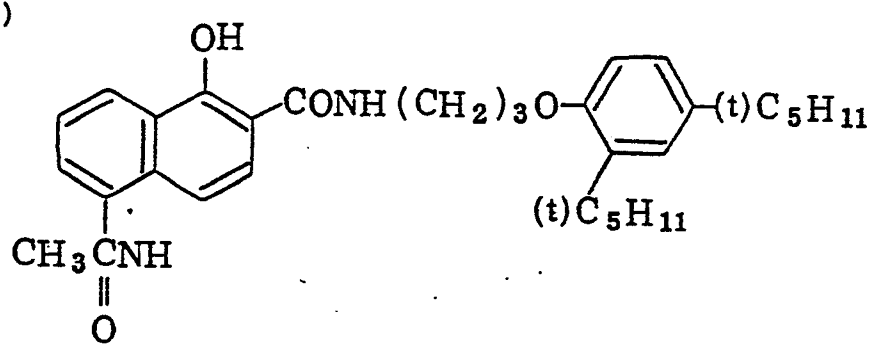
The polymeric coupler which can be used in the present invention can be prepared by polymerizing the vinyl monomer providing the repeating unit of formula (III), dissolving the resulting oleophilic polymer in an organic solvent, and dispersing the organic solution in a gelatin aqueous solution to form a latex. The process disclosed in U.S. Patent 3,451,820 may be applied to a dispersion of the oleophilic polymer in a gelatin aqueous solution. The polymeric coupler may also be prepared by direct emulsion polymerization in accordance with the process as disclosed in U.S. Patents 4,080,211 and 3,370,952.

Specific examples of the couplers represented by formula (I) including polymeric couplers are shown below for non-limiting illustrative purposes. In the following structural formulae, (t)C_5H_{11} represents $-C(CH_3)_2C_2H_5$ and (t)C_8H_{17} represents $-C(CH_3)_2CH_2C(CH_3)_3$.

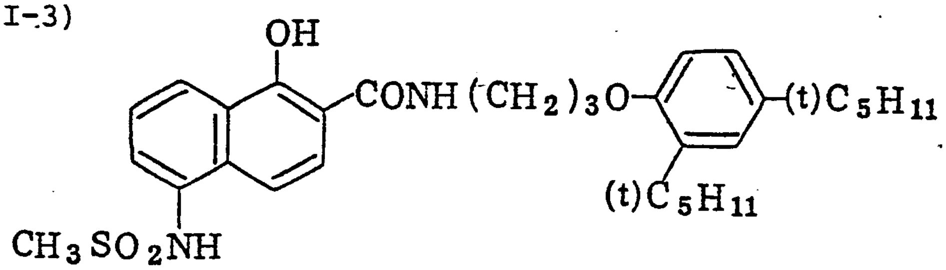
(I-1)


OH
CONH(CH2)3O
(t)C5H11
(t)C5H11
CF3CONH

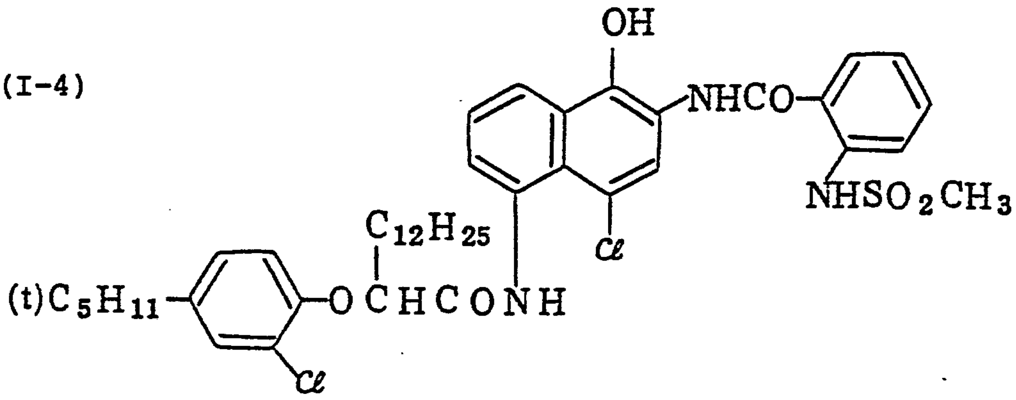
(I-2)


OH
CONH(CH2)3O
(t)C5H11
(t)C5H11
CH3CNH
O

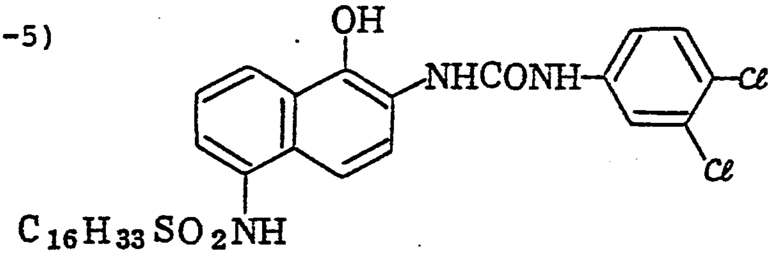
(I-3)


OH
CONH(CH2)3O
(t)C5H11
(t)C5H11
CH3SO2NH

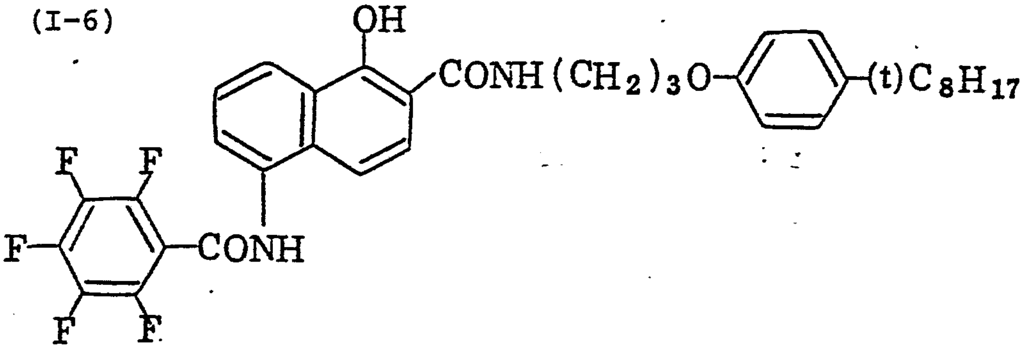
(I-4)


OH
NHCO
NHSO2CH3
C12H25
Cl
(t)C5H11
O CHCONH
Cl

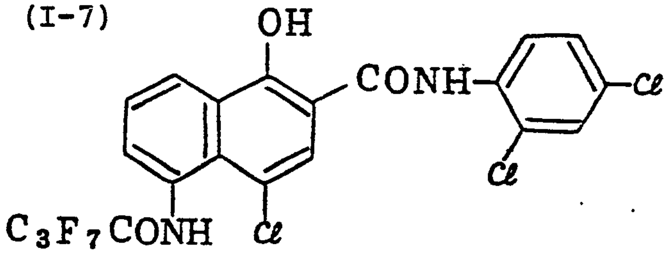
(I-5)


OH
NHCONH
Cl
Cl
C16H33SO2NH

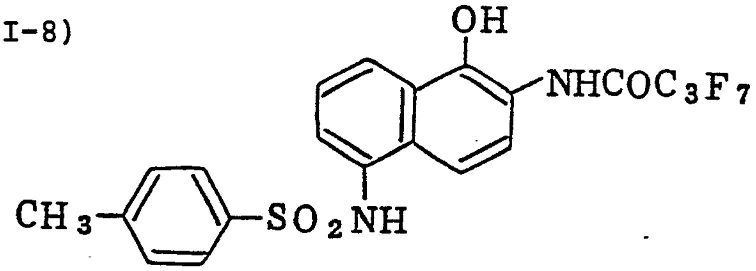
(I-6)


OH
CONH(CH2)3O
(t)C8H17
F
F
F
CONH
F
F

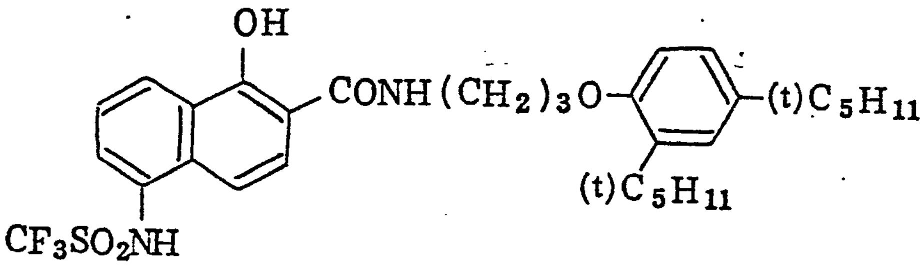
(I-7)



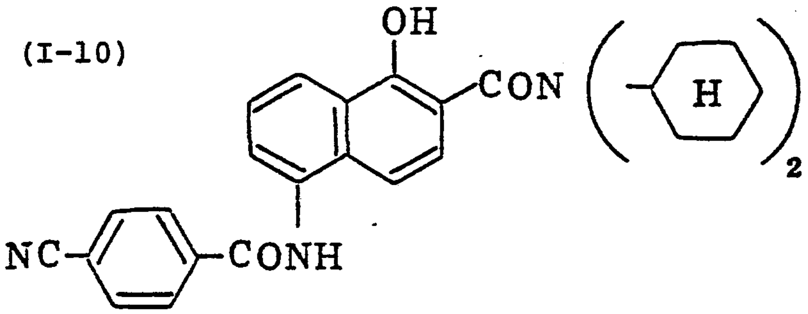
(I-8)



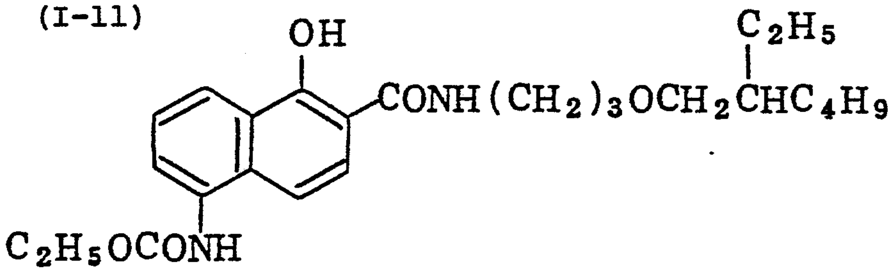
(I-9)



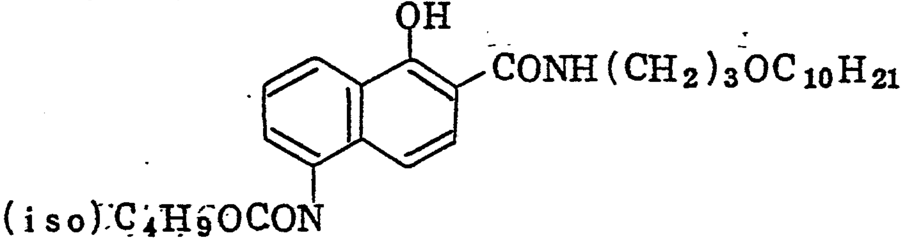
(I-10)


OH
CON
H
2
NC
CONH

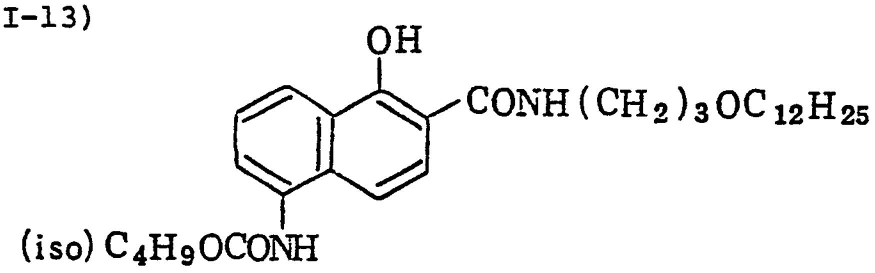
(I-11)


OH
C2H5
CONH(CH2)3OCH2CHC4H9
C2H5OCONH

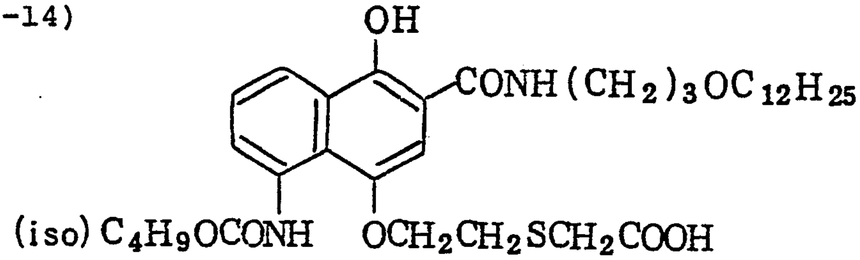
(I-12)


OH
CONH(CH2)3OC10H21
(iso)C4H9OCON

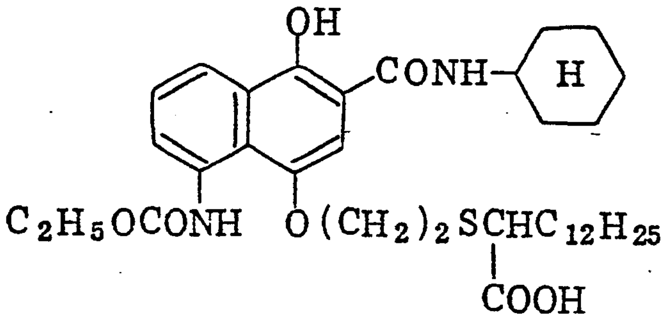
(I-13)


OH
CONH(CH2)3OC12H25
(iso) C4H9OCONH

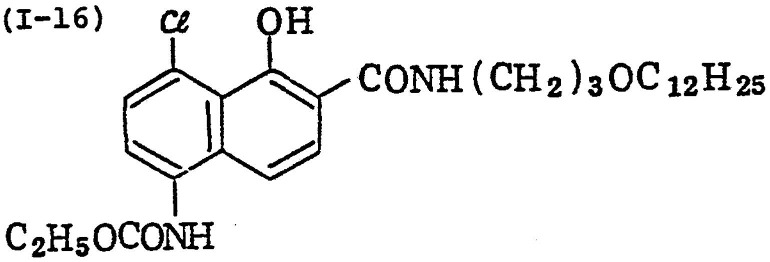
(I-14)


OH
CONH(CH2)3OC12H25
(iso) C4H9OCONH
OCH2CH2SCH2COOH

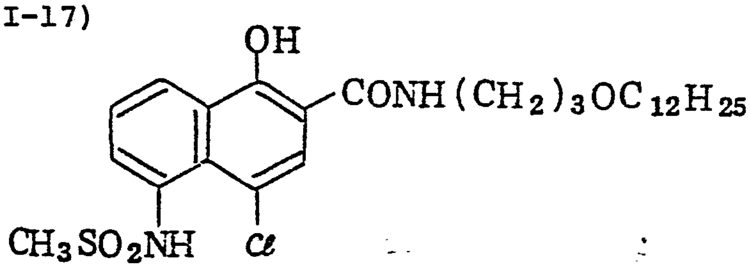
(I-15)


OH
CONH
H
C2H5OCONH
O(CH2)2SCHC12H25
COOH

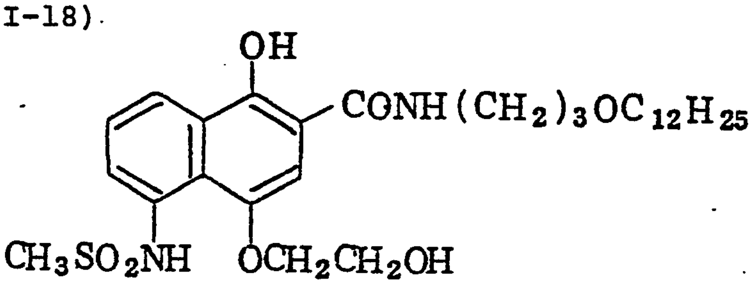
(I-16)


Cl
OH
CONH(CH2)3OC12H25
C2H5OCONH

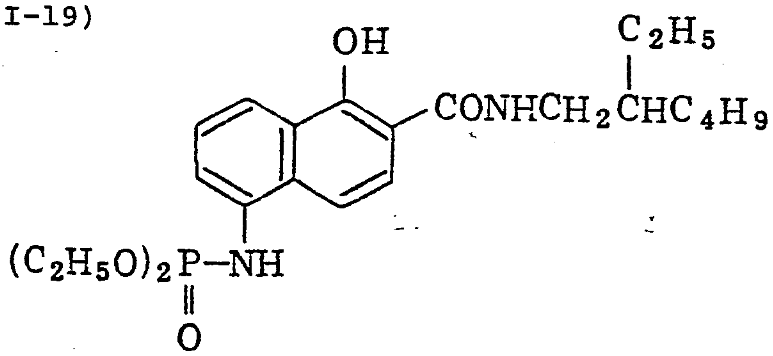
(I-17)


OH
CONH(CH2)3OC12H25
CH3SO2NH
Cl

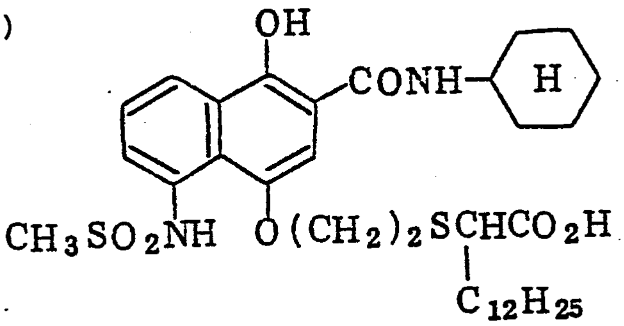
(I-18)


OH
CONH(CH2)3OC12H25
CH3SO2NH
OCH2CH2OH

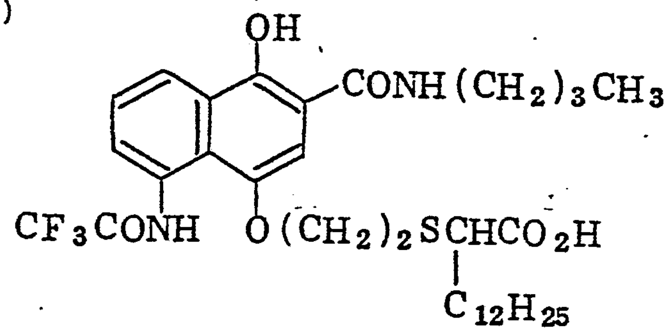
(I-19)


OH
C2H5
CONHCH2CHC4H9
(C2H5O)2P—NH
O

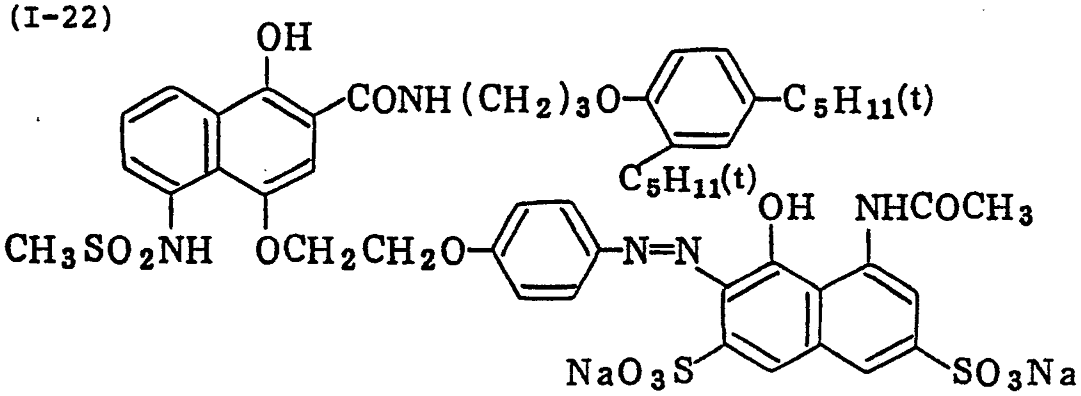
(I-20)


OH
CONH
H
CH3SO2NH
O(CH2)2SCHCO2H
C12H25

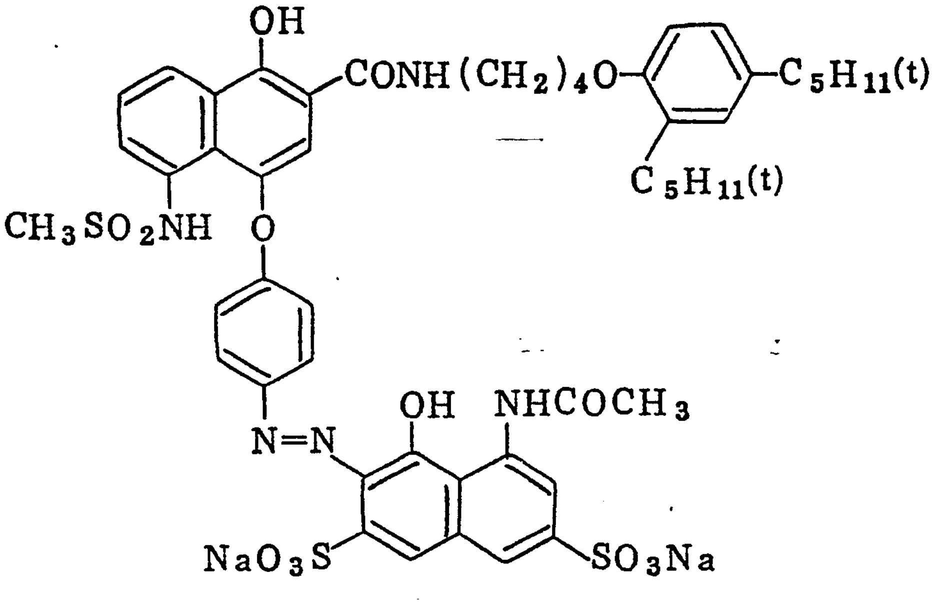
(I-21)


OH
CONH(CH2)3CH3
CF3CONH
O(CH2)2SCHCO2H
C12H25

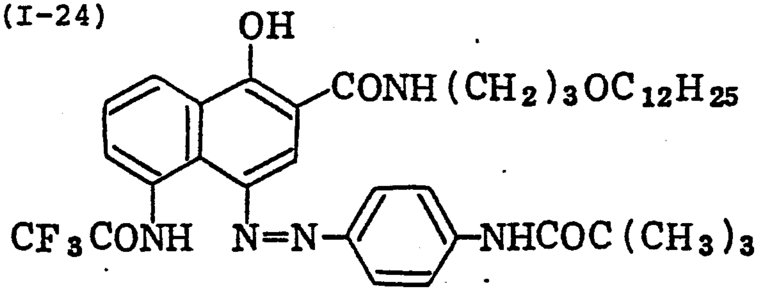
(I-22)


OH
CONH(CH2)3O
C5H11(t)
C5H11(t)
CH3SO2NH
OCH2CH2O
N=N
OH
NHCOCH3
NaO3S
SO3Na

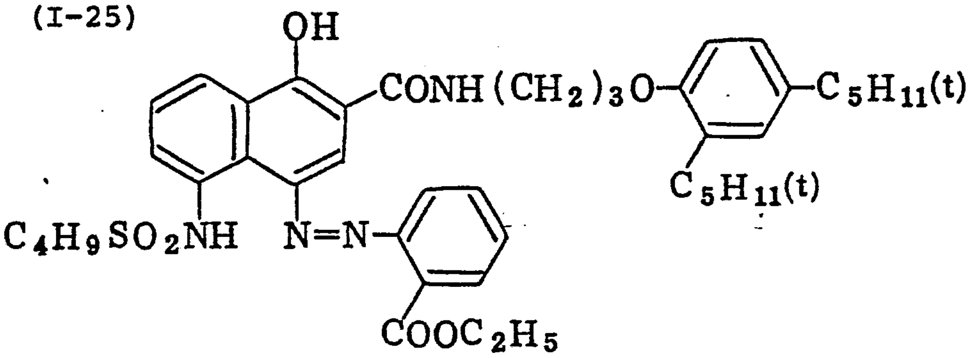
(I-23)


OH
CONH(CH2)4O
C5H11(t)
C5H11(t)
CH3SO2NH
O
N=N
OH
NHCOCH3
NaO3S
SO3Na

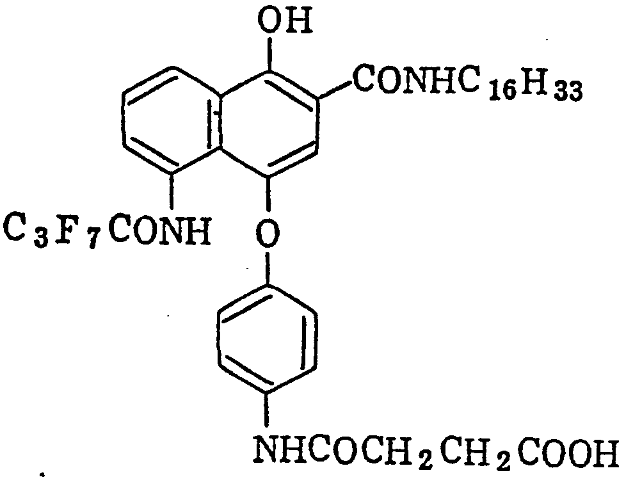
(I-24)


OH
CONH(CH2)3OC12H25
CF3CONH
N=N
NHCOC(CH3)3

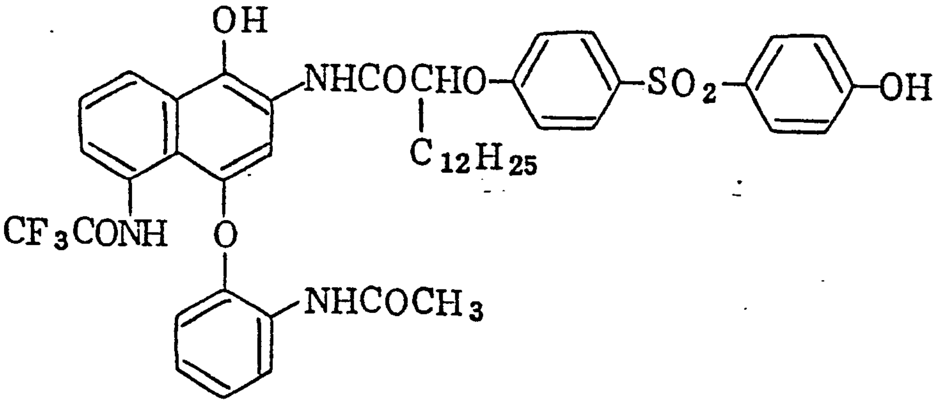
(I-25)


OH
CONH(CH2)3O
C5H11(t)
C5H11(t)
C4H9SO2NH
N=N
COOC2H5

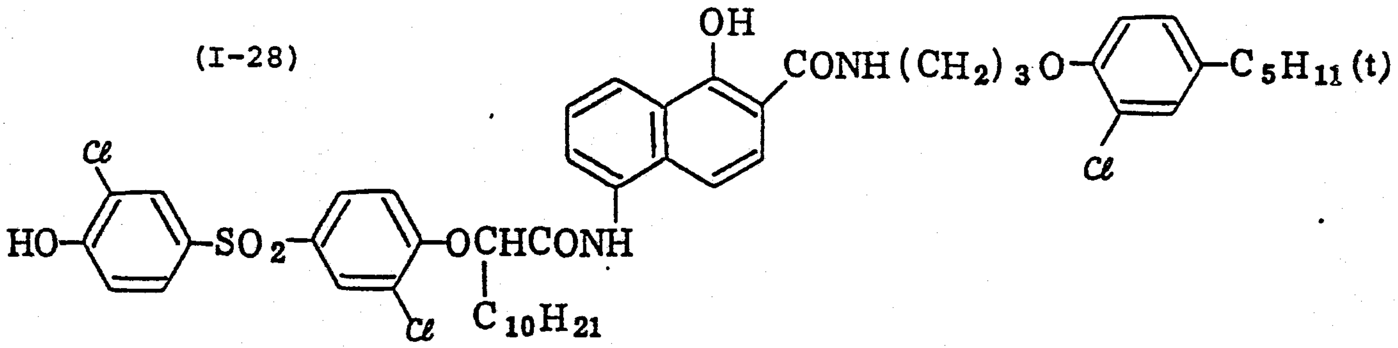
(I-26)


OH
CONHC16H33
C3F7CONH
O
NHCOCH2CH2COOH

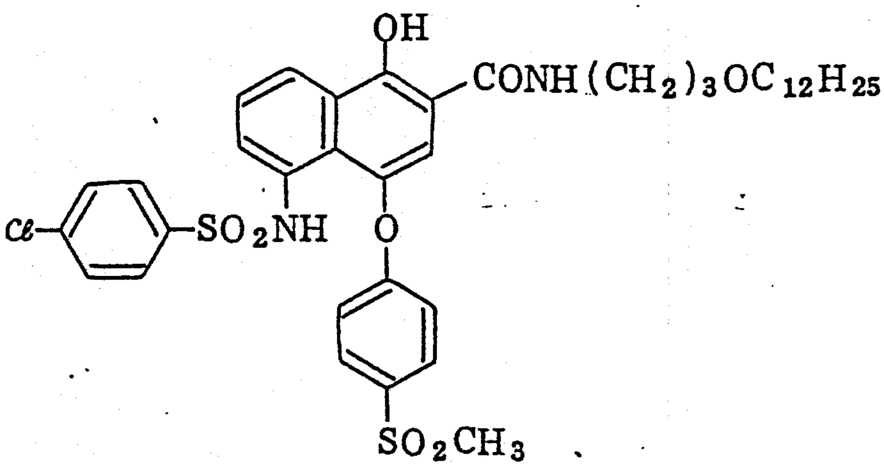
(I-27)


OH
NHCOCHO
C12H25
SO2
OH
CF3CONH
O
NHCOCH3

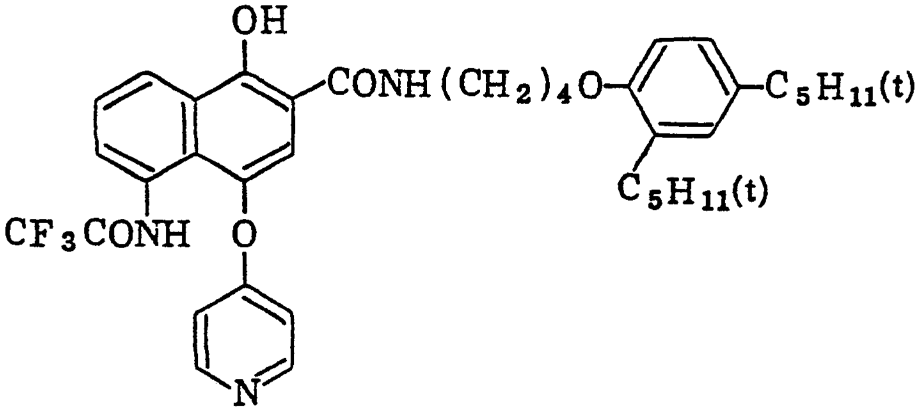
(I-28)


OH
CONH(CH2)3O
C5H11(t)
Cl
Cl
HO
SO2
OCHCONH
C10H21
Cl

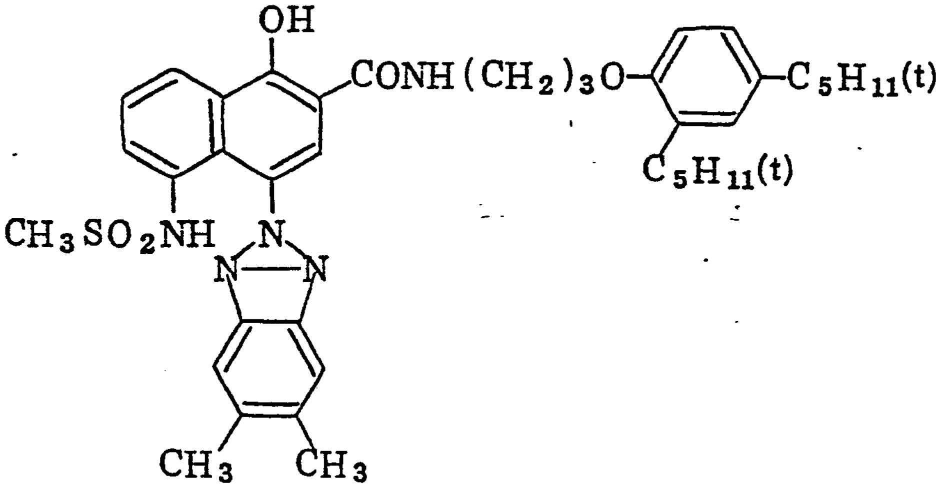
(I-29)


OH
CONH(CH2)3OC12H25
Cl
SO2NH
O
SO2CH3

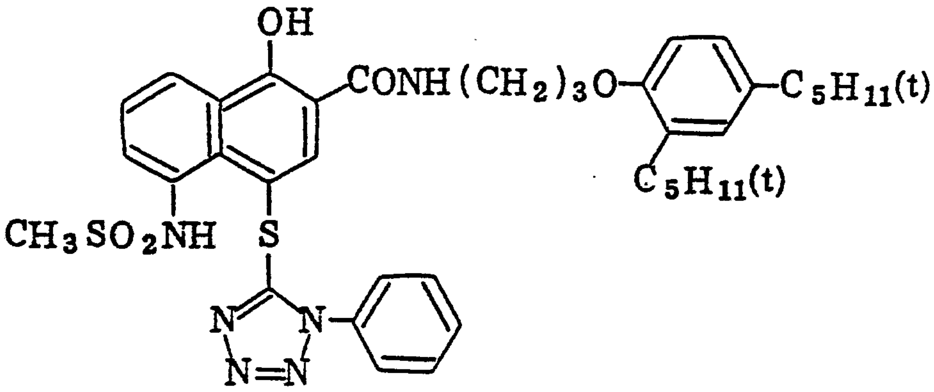
(I-30)


OH
CONH(CH2)4O
C5H11(t)
C5H11(t)
CF3CONH
O
N

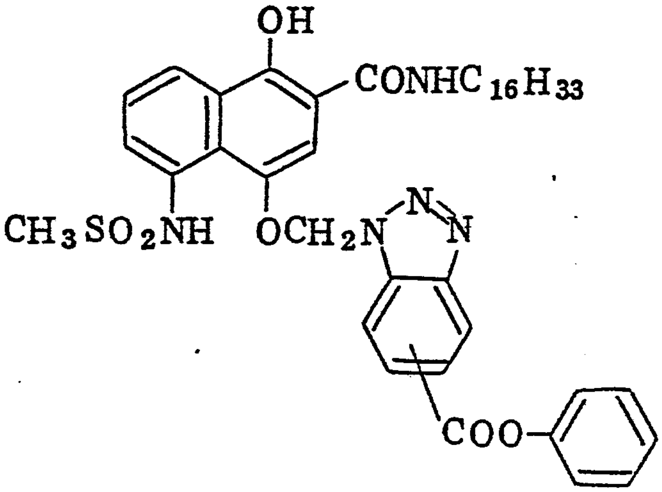
(I-31)


OH
CONH(CH2)3O
C5H11(t)
C5H11(t)
CH3SO2NH
N
N
N
CH3
CH3

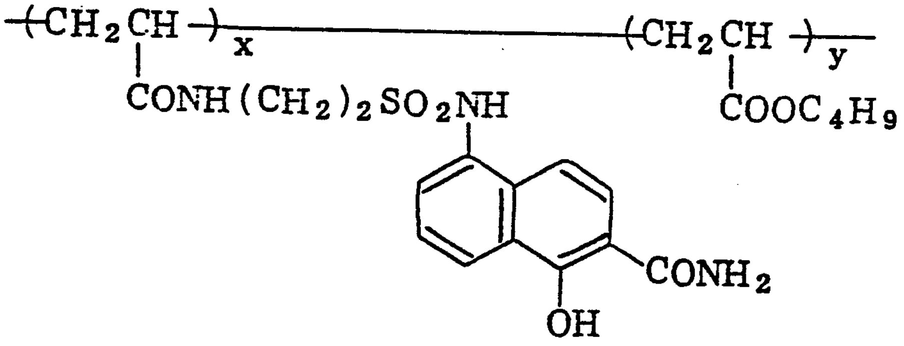
(I-32)


OH
CONH(CH2)3O
C5H11(t)
C5H11(t)
CH3SO2NH
S
N
N
N=N

(I-33)

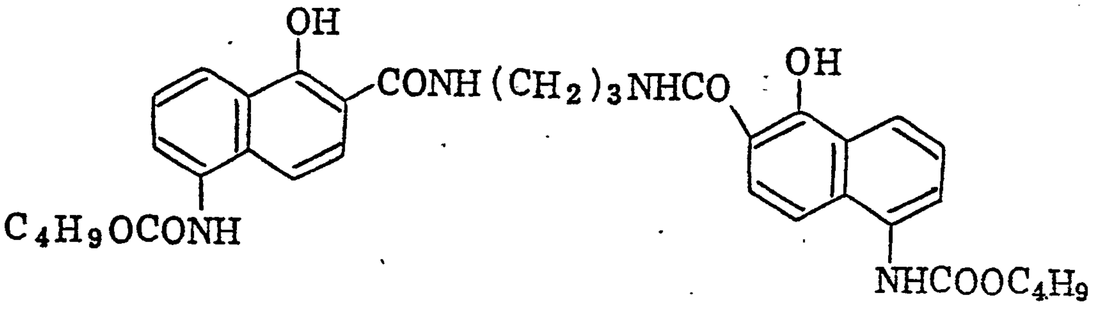

OH
CONHC16H33
CH3SO2NH
OCH2N
N
N
COO

(I-34)

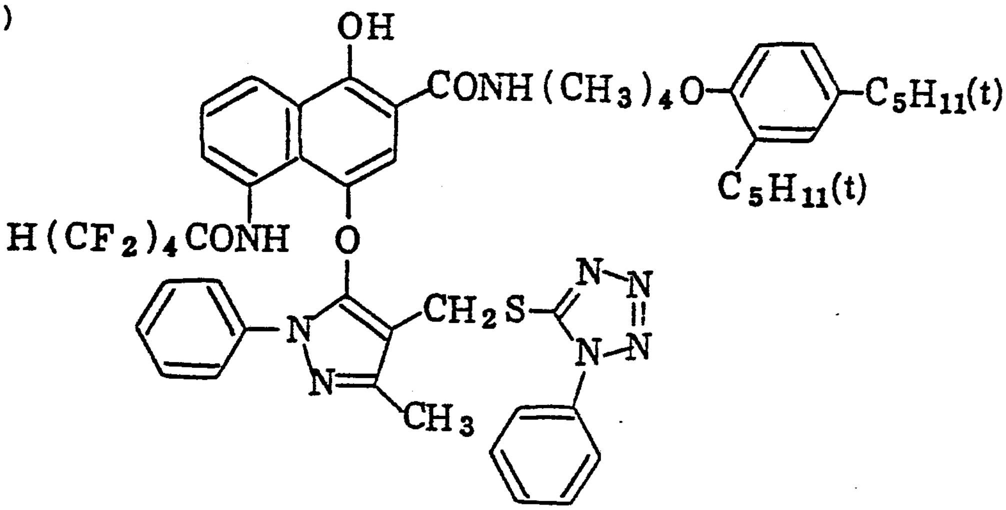


$x / y = 80 / 20$ (molar ratio)

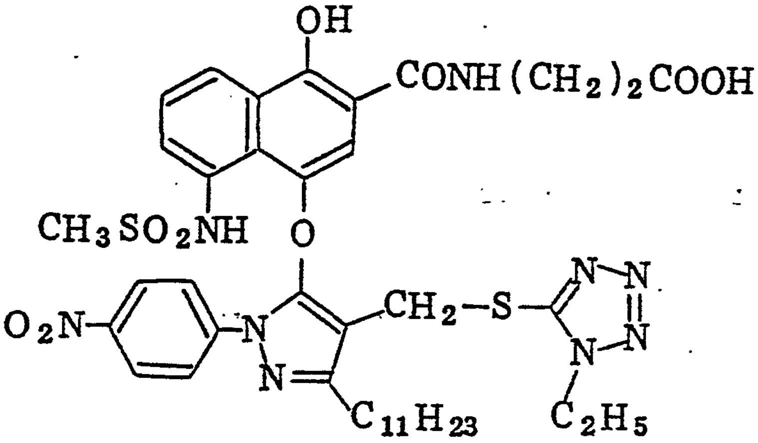
(I-35)



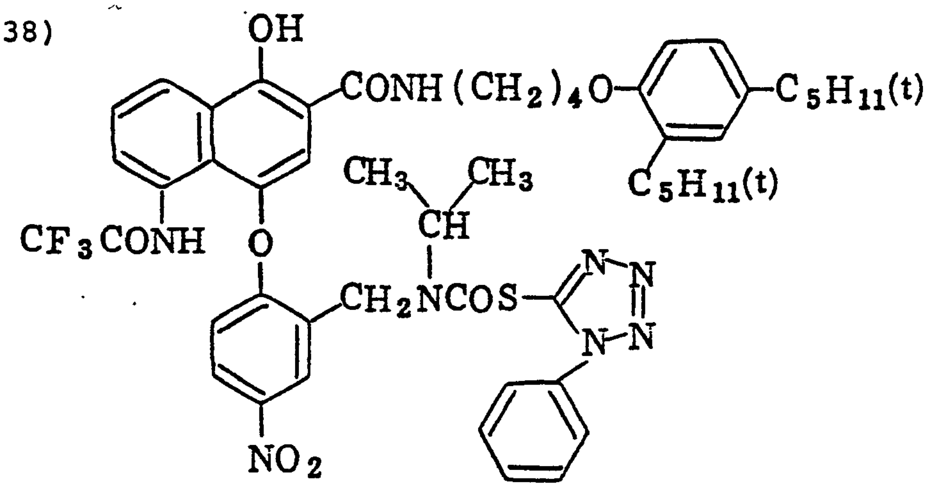
(I-36)


OH
CONH(CH3)4O
C5H11(t)
C5H11(t)
H(CF2)4CONH
O
CH2S
N
N
N
N
N
N
CH3

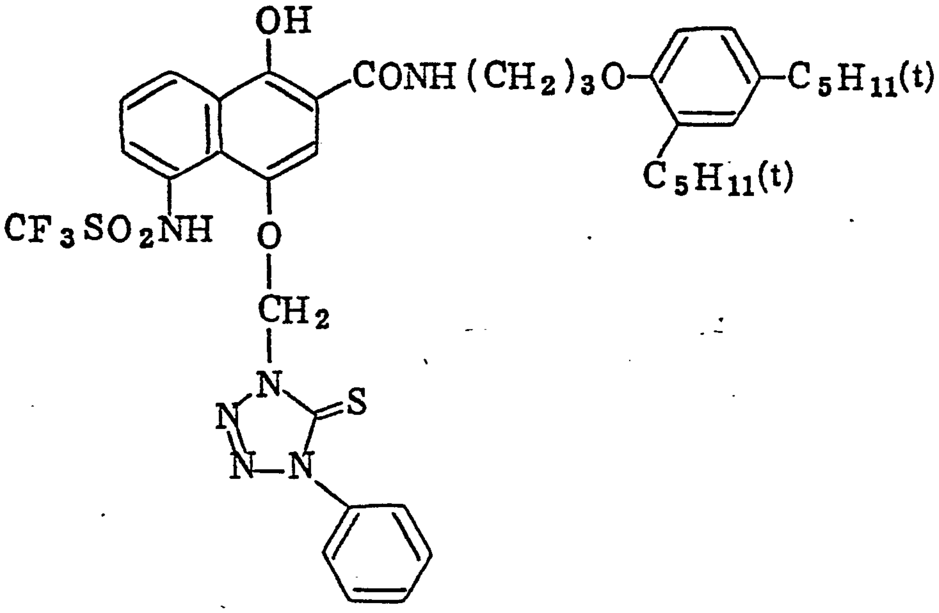
(I-37)


OH
CONH(CH2)2COOH
CH3SO2NH
O
O2N
N
N
CH2—S
N
N
N
N
C11H23
C2H5

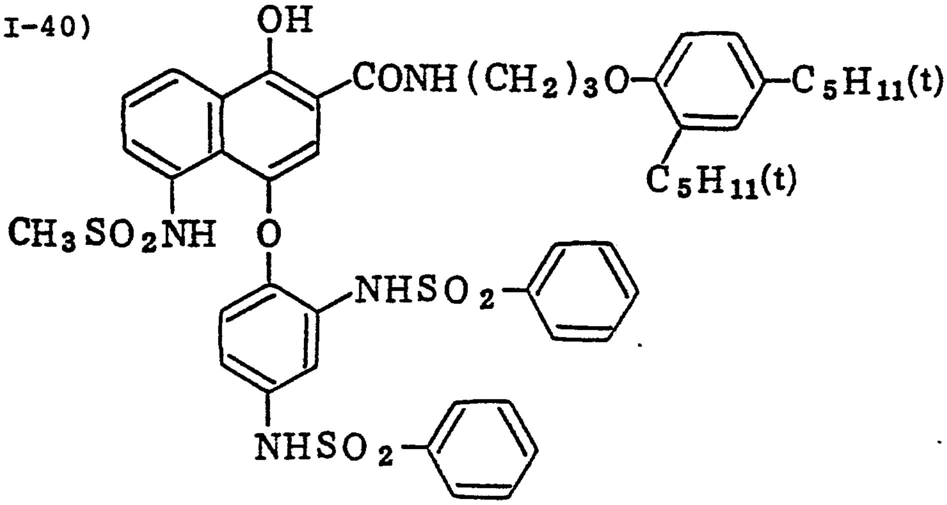
(I-38)


OH
CONH(CH₂)₄O
C₅H₁₁(t)
C₅H₁₁(t)
CH₃
CH₃
CH
CF₃CONH
O
CH₂NCOS
N
N
N
N
NO₂

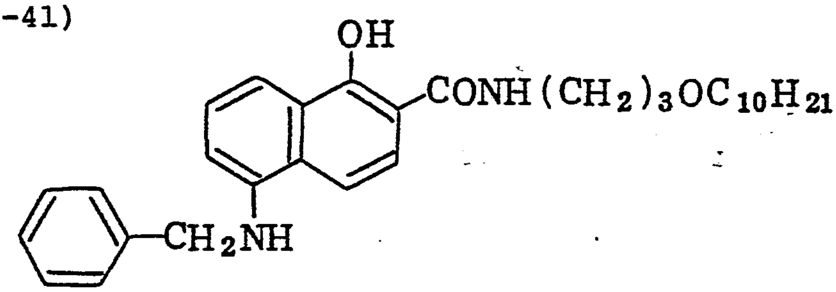
(I-39)


OH
CONH(CH₂)₃O
C₅H₁₁(t)
C₅H₁₁(t)
CF₃SO₂NH
O
CH₂
N
S
N
N
N

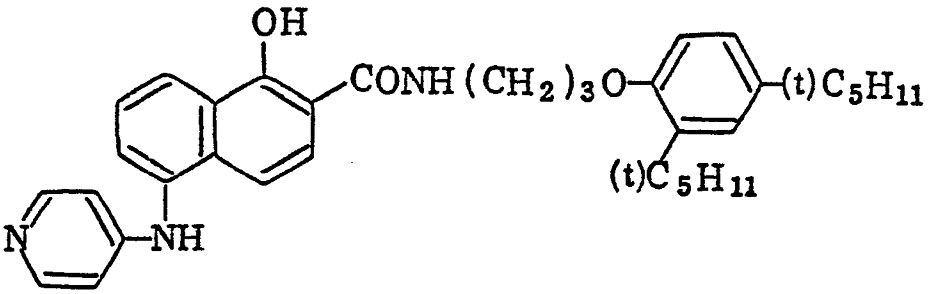
(I-40)


OH
CONH(CH2)3O
C5H11(t)
C5H11(t)
CH3SO2NH
O
NHSO2
NHSO2

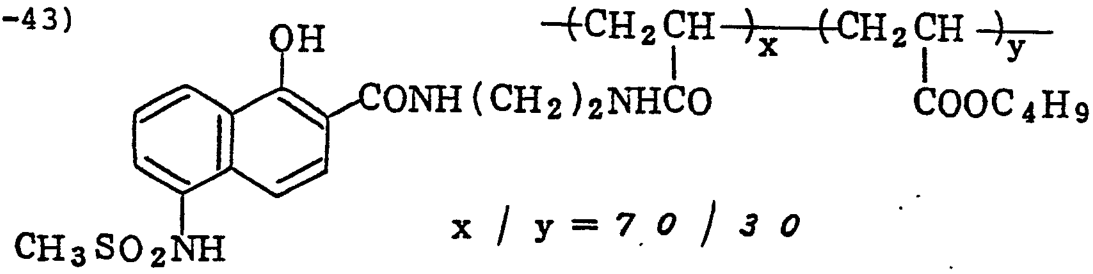
(I-41)


OH
CONH(CH2)3OC10H21
CH2NH

(I-42)

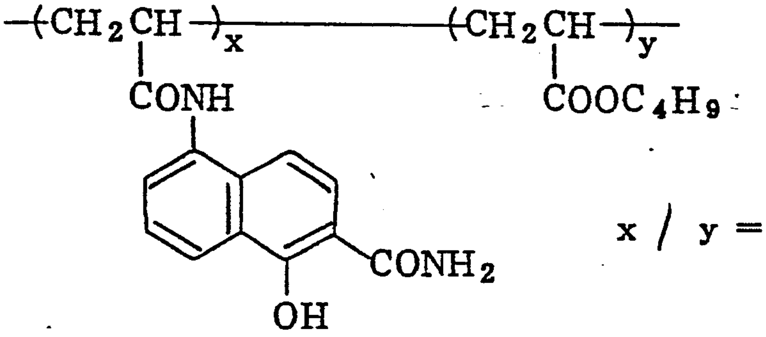


(I-43)



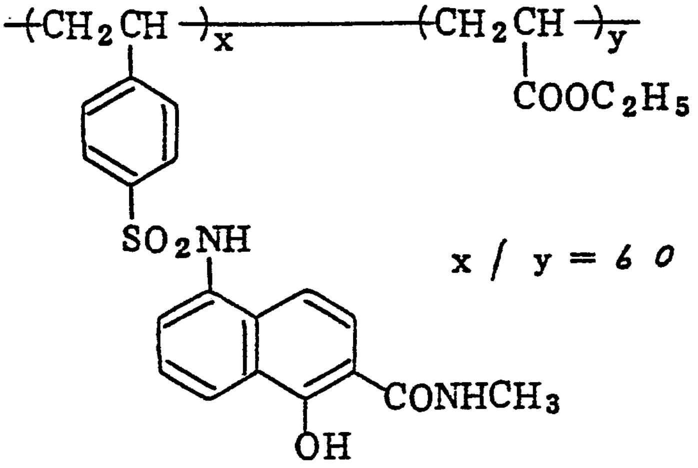
x / y = 70 / 30

(I-44)



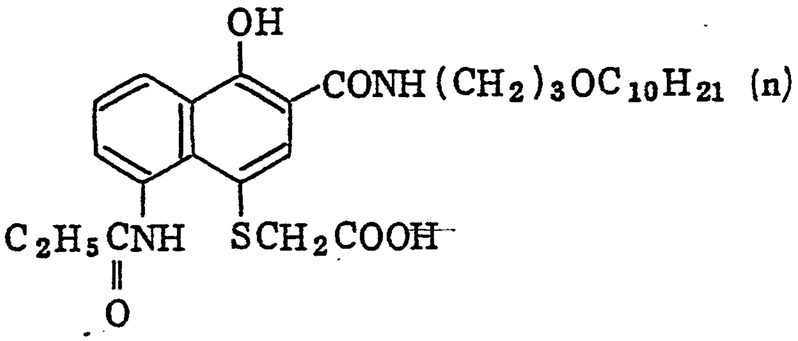
x / y = 50 / 50

(I-45)

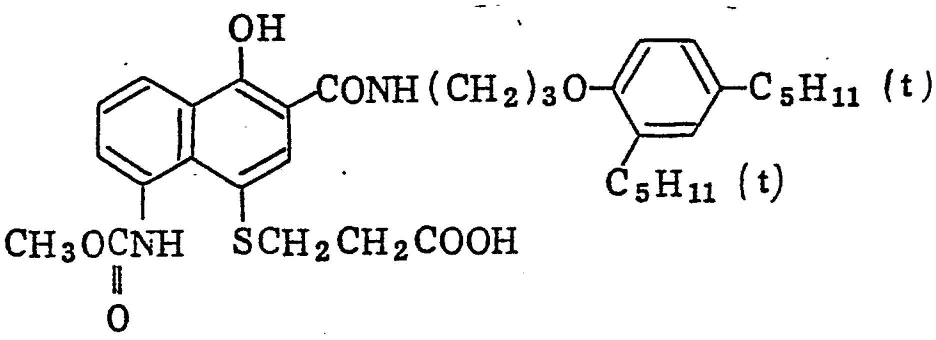


x / y = 60 / 40

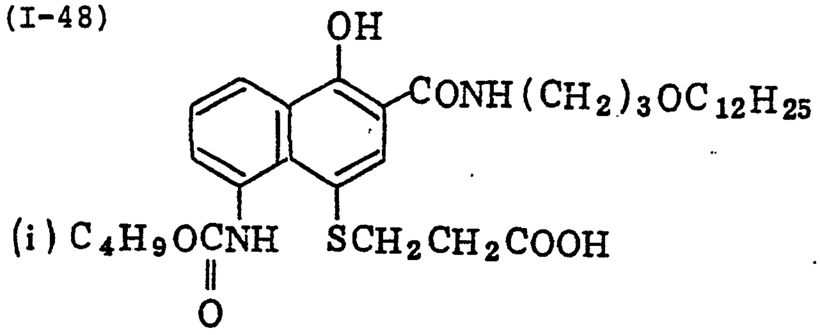
(I-46)



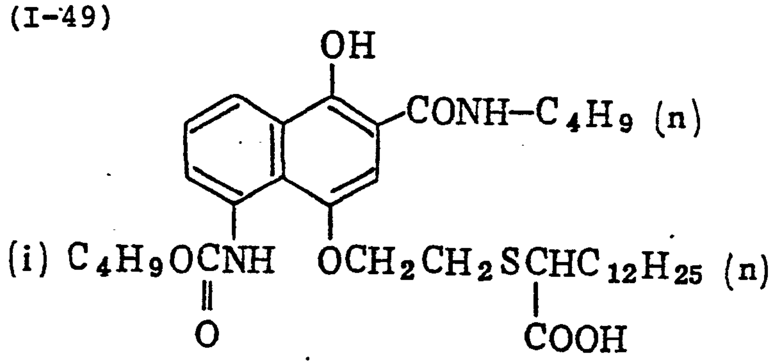
(I-47)



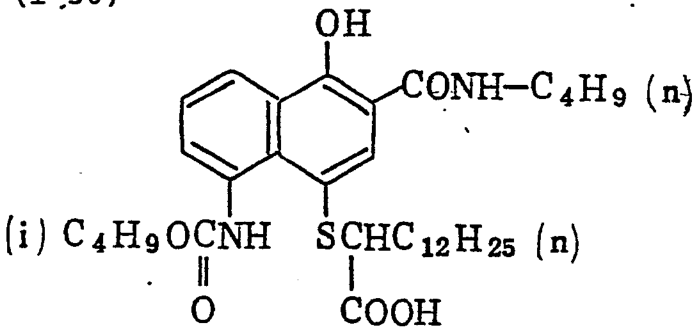
(I-48)



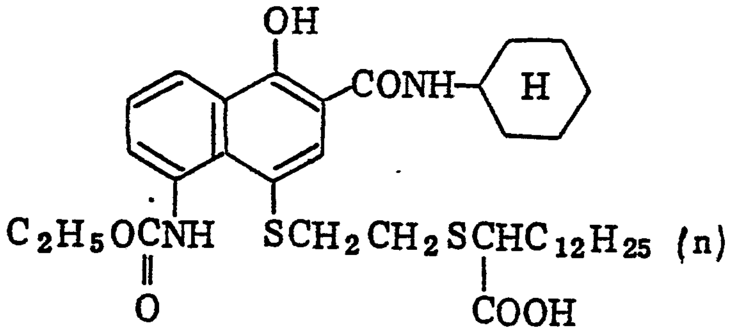
(I-49)



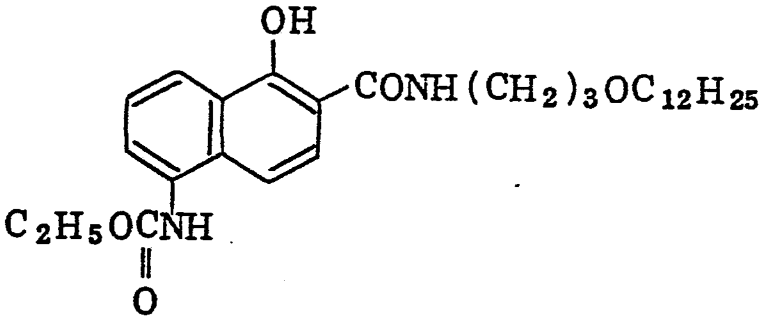
(I-50)



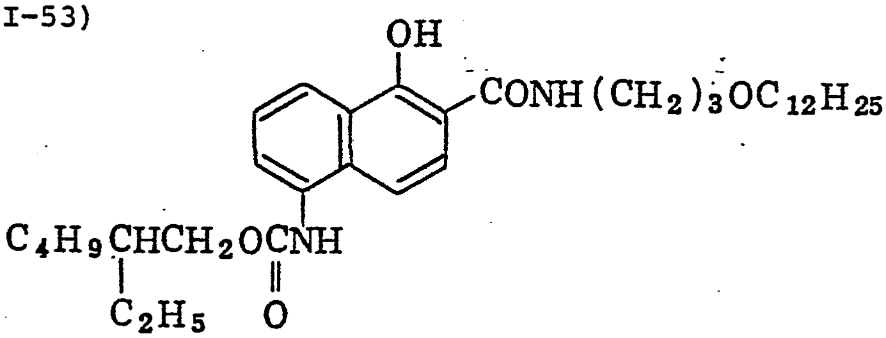
(I-51)


OH
CONH
H
C_2H_5OCNH
O
$SCH_2CH_2SCHC_{12}H_{25}$ (n)
COOH

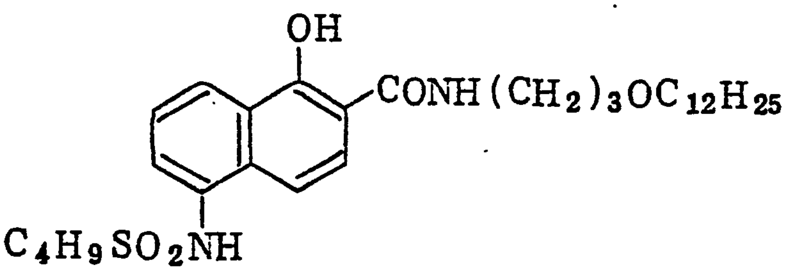
(I-52)


OH
$CONH(CH_2)_3OC_{12}H_{25}$
C_2H_5OCNH
O

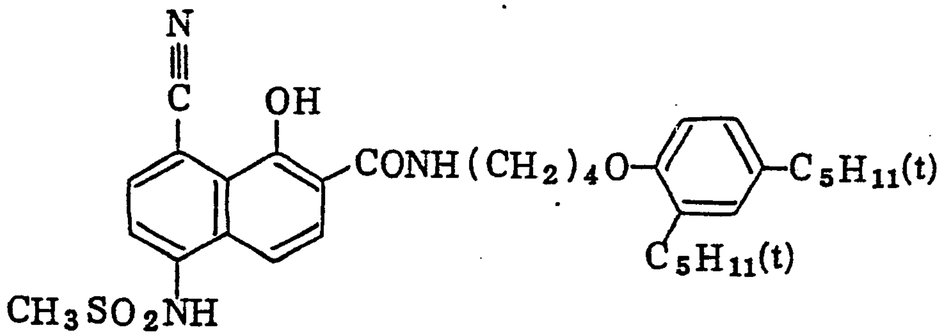
(I-53)


OH
$CONH(CH_2)_3OC_{12}H_{25}$
$C_4H_9CHCH_2OCNH$
C_2H_5
O

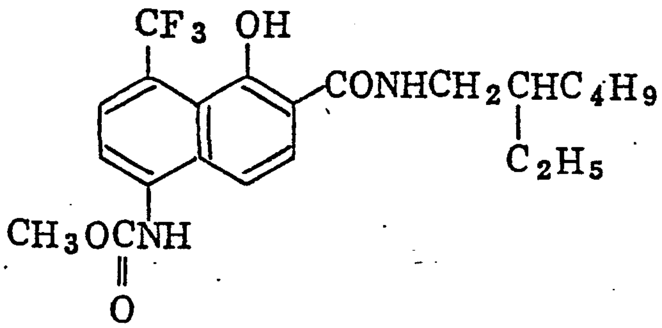
(I-54)



(I-55)



(I-56)



The couplers represented by formula (I) can be synthesized easily in accordance with the process described in European Patent 161626A.

The high-boiling point organic solvents which can be used in the present invention are those having a boiling point of 175°C or higher at normal pressure (760 mmHg).

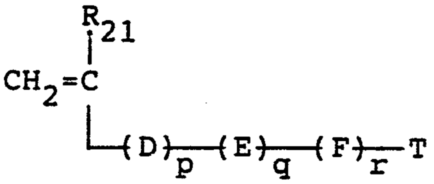
Examples of the high-boiling point organic solvents which can be used in combination with the couplers of formula (I) include phosphoric esters, e.g., triphenyl phosphate, tricresyl phosphate, octyldiphenyl phosphate, tri-2-ethylhexyl phosphate, tri-n-hexyl phosphate, tri-iso-nonyl phosphate, tricyclohexyl phosphate, tributoxyethyl phosphate, tri-2-chloroethyl phosphate, etc.; benzoic esters, e.g., 2-ethylhexyl benzoate, 2-ethylhexyl 2,4-dichlorobenzoate, etc.; fatty acid esters, e.g., di-2-ethylhexyl succinate, 2-hexyldecyl tetradecanoate, tributyl citrate, etc.; amides, e.g., N,N-diethyldodecanamide, N-tetradecylpyrrolidone, etc.; dialkylanilines, e.g., 2-butoxy-5-t-octyl-N,N-dibutylaniline, etc.; chlorinated paraffins, i.e., paraffins having a chlorine content of from 10 to 80% by weight; phenols, e.g., 2,5-di-t-amylphenol, 2,5-di-t-hexyl-4-methoxyphenol, 2-ethylhexyl p-hydroxybenzoate, etc.; phthalic esters, e.g., dibutyl phthalate, dicyclohexyl phthalate, diheptyl phthalate, di-2-ethylhexyl phthalate, didodecyl phthalate, etc.; and the like. Preferred among them are phosphoric esters and phthalic esters.

The amount of the high-boiling point organic solvent to be used in this invention should not exceed 0.3 g per gram of the coupler of formula (I) (i.e., it should not exceed 30 wt%). If it exceeds 0.3 g/g-coupler, sharpness is conspicuously deteriorated. A preferred amount of the high-boiling point solvent is 0.15 g or less, more preferably 0.05 g or less, and most preferably 0.01 g or less, per gram of the coupler. The high-boiling point organic solvent may not be used at all. In this case, the coupler is emulsified in the hydrophilic colloid by using a low-boiling point organic solvent (having a boiling point of from about 30°C to about 160°C, such as 2-ethoxyethyl acetate, N,N-dimethylformamide, etc.)

The amount of the cyan coupler represented by formula (I) usually ranges from 1.0×10^{-5} to 3.0×10^{-3} mol/m^2, and preferably from 5.0×10^{-5} to 1.5×10^{-3} mol/m^2.

When the silver halide color photographic material according to the present invention contains two or more silver halide emulsion layers being sensitive to the same color but differing in sensitivity, the present invention is preferably applied to layers other than the layer having the highest sensitivity.

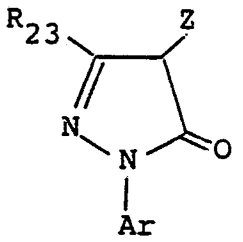
The magenta couplers which can be used in the present invention are preferably polymeric magenta couplers, and more preferably those obtained from a monomer represented by formula (IV)



$$CH_2=\underset{\lfloor (D)_p-(E)_q-(F)_r-T}{\overset{R_{21}}{C}} \qquad (IV)$$

wherein R_{21} represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms or a chlorine atom; D represents -COO-, -CONR$_{22}$-or a substituted or unsubstituted phenyl group; E represents a substituted or unsubstituted alkylene, phenylene or aralkylene group having from 1 to 10 carbon atoms; F represents -CONR$_{22}$-, -NR$_{22}$CONR$_{22}$-, -NR$_{22}$COO-, -NR$_{22}$CO-, -OCONR$_{22}$-, -NR$_{22}$-, -COO-, -OCO-, -CO-, -O-, -S-, -SO$_2$-, -NR$_{22}$SO$_2$-or -SO$_2$NR$_{22}$-, wherein R_{22} represents a hydrogen atom or a substituted or unsubstituted aliphatic or aryl group, a plurality of R_{22}, if any, may be the same or different; p, q, and r each represents 0 or 1 provided that at least one of them is 1; and T represents a coupler residual group derived from a magenta coupler represented by formula (V) shown below.

Formula (V) is represented by



(V)

wherein Ar represents an alkyl group, an aryl group, and a heterocyclic group; R_{23} represents a substituted or unsubstituted anilino group, a substituted or unsubstituted acylamino group (e.g., an alkylcarbonamido group, a phenylcarbonamido group, an alkoxycarbonamido group, a phenyloxycarbonaido group, etc.), a substituted or unsubstituted ureido group (e.g., an alkylureido group, a phenylureido group, etc.) or a substituted or unsubstituted sulfonamido group; and Z represents a hydrogen atom, a halogen atom (e.g., a chlorine atom, a bromine atom, etc.), a coupling releasable group bonded via an oxygen atom (e.g., an acetoxy group, a propanoyloxy group, a benzoyloxy group, an ethoxyoxaloyloxy group, a pyruvoyloxy group, a cinnamoyloxy group, a phenoxy group, a 4-cyanophenoxy group, a 4-ethanesulfonamidophenoxy group, an α-naphthoxy group, a 4-cyanoxy group, a 4-methanesulfonamidophenoxy group, a 3-pentadecylphenoxy group, a benzyloxycarbonyloxy group, an ethoxy group, a 2-cyanoethoxy group, a benzyloxy group, a 2-phenethyloxy group, a 2-phenoxyethoxy group, a 5-phenyltetrazolyloxy group, a 2-benzothiazolyloxy group, etc.), a coupling releasable group bonded via a nitrogen atom (e.g., those described in British Patent Application No. 2,132,783, e.g., a benzenesulfonamido group, an N-ethyltoluenesulfonamido group, a heptafluorobutaneamido group, a 2,3,4,5,6-pentafluorobenzamido group, an octanesulfonamido group, a p-cyanophenylureido group, an N,N-diethylsulfamoylamino group, a 1-piperidyl group, a 5,5-dimethyl-2,4-dioxo-3-oxazolidinyl group, a 1-benzyl-5-ethoxy-3-hydantoinyl group, a 2-oxo-1,2-dihydro-1-pyridinyl group, an imidazolyl group, a pyrazolyl group, a 3,5-diethyl-1,2,4-triazol-1-yl group, a 5-or 6-bromobenzotriazol-1-yl group, a 5-methyl-1,2,3,4-triazol-1-yl group, a benzimidazolyl group, etc.) or a coupling releasable group bonded via a sulfur atom (e.g., a phenylthio group, a 2-carboxyphenylthio group, a 2-methoxy-5-octylphenylthio group, a 4-methanesulfonylphenylthio group, a 4-octanesulfonamidophenylthio group, a benzylthio group, a 2-cyanoethylthio group, a 5-phenyl-2,3,4,5-tetrazolylthio group, a 2-benzothiazolyl group, etc.).

In the monomer of the formula (IV), the coupler residual group T of formula (V) is bonded to (D) (E) (F) at any of Ar, X, and R_{23}.

In formula (V), the group as represented by Ar includes a substituted or unsubstituted alkyl group (the substituent includes a halogen atom, a cyano group, a benzyl group, etc.), a substituted or unsubstituted heterocyclic group (e.g., a 4-pyridyl group, a 2-thiazoyl group, etc.), and a substituted or unsubstituted aryl group. The substituent for the heterocyclic group or aryl group includes an alkyl group (e.g., a methyl group, an ethyl group, etc.), an alkoxy group (e.g., a methoxy group, an ethoxy group, etc.), an aryloxy group (e.g., a phenyloxy group, etc.), an alkoxycarbonyl group (e.g., a methoxycarbonyl group, etc.), an acylamino group (e.g., an acetylamino group, etc.), a carbamoyl group, an alkylcarbamoyl group (e.g., a methylcarbamoyl group, an ethylcarbamoyl group, etc.), a dialkylcarbamoyl group (e.g., a dimethylcarbamoyl group, etc.), an arylcarbamoyl group (e.g., a phenylcarbamoyl group, etc.), an alkylsulfonyl group (e.g., a methylsulfonyl group, etc.), an arylsulfonyl group (e.g., a phenylsulfonyl group, etc.), an alkylsulfonamido group (e.g., a methanesulfonamido group, etc.), an arylsulfonamido group (e.g., a phenylsulfonamido group, etc.), a sulfamoyl group, an alkylsulfamoyl group (e.g., an ethylsulfamoyl group, etc.), a dialkyl sulfamoyl group (e.g., a dimethylsulfamoyl group, etc.), an alkylthio group (e.g., a methylthio group), an arylthio group (e.g., a phenylthio group, etc.), a cyano group, a nitro group, a halogen atom (e.g., a fluorine atom, a chlorine atom, a bromine atom, etc.), and the like. When two or more of these groups substitute the heterocyclic or aryl group, they may be the same or different. Preferred among these substituents are a halogen atom, an alkyl group, an alkoxy group, an alkoxycarbonyl group, and a cyano group.

The substituent for the group as represented by R_{23} includes a halogen atom (e.g., a fluorine atom, a chlorine atom, a bromine atom, etc.), a straight or branched chain alkyl group (e.g., a methyl group, a t-butyl group, an octyl group, a tetradecyl group, etc.), an alkoxy group (e.g., a methoxy group, an ethoxy group, a 2-ethylhexyloxy group, a tetradecyloxy group, etc.), an acylamino group (e.g., an acetamido group, a benzamido group, a butanamido group, an octanamido group, a tetradecanamido group, an α-(2,4-di-t-amylphenoxy)acetamido group, an α-(2,4-di-t-amylphenoxy)butylamido group, an α-(3-pentadecylphenoxy)-hexanamido group, an α-(4-hydroxy-3-t-butylphenoxy)tetradecanamido group, a 2-oxo-pyrrolidin-1-yl group, a 2-oxo-5-tetradecylpyrrolidin-1-yl group, an N-methyltetradecanamido group, etc.), a sulfonamido group (e.g., a methanesulfonamido group, a benzenesulfonamido group, an ethylsulfonamido group, a p-toluenesulfonamido group, an octanesulfonamido group, a p-dodecylbenzenesulfonamido group, an N-methyltetradecanesulfonamido group, etc.), a sulfamoyl group (e.g., a sulfamoyl group, an N-methylsulfamoyl group, an N-ethylsulfamoyl group, an N,N-dimethylsulfamoyl group, an N,N-dihexylsulfamoyl group, an N-hexadecyluslfamoyl group, an N-[3-(dodecyloxy)propyl]sulfamoyl group, an N-[4-(2,4-di-t-amylphenoxy)butyl]sulfamoyl group, an N-methyl-N-tetradecylsulfmaoyl group, etc.), a carbamoyl group (e.g., an N-methylcarbamoyl group, an N-butylcarbamoyl group, an N-octadecylcarbamoyl group, an N-[4-(2,4-di-t-amylphenoxy)butyl]carbamoyl group, an N-methyl-N-tetradecylcarbamoyl group, etc.), a diacylamino group (e.g., an N-succinimido group, an N-phthalimido group, a 2,5-dioxo-1-oxazolidinyl group, a 3-dodecyl-2,5-dioxo-1-hydantoinyl group, a 3-(N-acetyl-N-dodecylamino)succinimido group, etc.), an alkoxycarbonyl group (e.g., a methoxycarbonyl group, a tetradecyloxycarbonyl group, a benzyloxycarbonyl group, etc.), an alkoxysulfonyl group (e.g., a methoxysulfonyl group, a butoxysulfonyl group, an octyloxysulfonyl group, a tetradecyloxysulfonyl group, etc.), an aryloxysulfonyl group (e.g., a phenoxysulfonyl group, a p-methylphenoxysulfonyl group, a 2,4-di-t-amylphenoxysulfonyl group, etc.), an alkanesulfonyl group (e.g., a methanesulfonyl group, an ethanesulfonyl group, an octanesulfonyl group, a 2-ethylhexylsulfonyl group, a hexadecanesulfonyl group, etc.), an arylsulfonyl group (e.g., a benzenesulfonyl group, a 4-nonylbezenesulfonyl group, etc.), an alkylthio group (e.g., a methylthio group, an ethylthio group, a hexylthio group, a benzylthio group, a tetradecylthio group, a 2-(2,4-di-t-amylphenoxy)ethylthio group, etc.), an arylthio group (e.g., a phenylthio group, a p-tolylthio group, etc.), an alkyloxycarbonylamino group (e.g., a methoxycarbonylamino group, an ethoxycarbonylamino group, a benzyloxycarbonylamino group, a hexadecyloxycarbonylamino group, etc.), an alkylureido group (e.g., an N-methylureido group, an N,N-dimethylureido group, an N-methyl-N-dodecylureido group, an N-hexadecylureido group, an N,N-dioctadecylureido group, etc.), an acyl group (e.g., an acetyl group, a benzoyl group, an octadecanoyl group, a p-dodecanamidobenzoyl group, etc.), a nitro group, a carboxyl group, a sulfo group, a hydroxyl group, a trichloromethyl group, and the like. The alkyl moiety and the aryl moiety of the above-enumerated substituents have a carbon atom number of from 1 to 36 and from 6 to 38, respectively.

Z preferably represents a coupling releasable group bonded at a nitrogen atom, and more preferably a pyrazolyl group.

The alkylene group as represented by E in formula (IV) may have either a straight chain or a branched chain. Examples of the alkylene group are a methylene group, a methylmethylene group, a dimethylmethylene group, a dimethylene group, a trimethylene group, a tetramethylene group, a pentamethylene group, a hexamethylene group, a decylmethylene group, etc. Examples of the aralkylene group as represented by E are a benzylidene group, and the phenylene group as represented by E are a p-phenylene group, an m-phenylene group, a methylphenylene group, etc.

The substituents for these groups as E include an aryl group (e.g., a phenyl group, etc.), a nitro group, a hydroxyl group, a cyano group, a sulfo group, an alkoxy group (e.g., a methoxy group, etc.), an aryloxy group (e.g., a phenoxy group, etc.), an acyloxy group (e.g., an acetoxy group, etc.), an acylamino group (e.g., an acetylamino group, etc.), a sulfonamido group (e.g., a methanesulfonamido group, etc.), a sulfamoyl group (e.g., a methylsulfamoyl group, etc.), a halogen atom (e.g., a fluorine atom, a chlorine atom, a bromine atom, etc.), a carboxyl group, a carbamoyl group (e.g., a methylcarbamoyl group, etc.), an alkoxycarbonyl group (e.g., a methoxycarbonyl group, etc.), a sulfonyl group (e.g., a methylsulfonyl group, etc.), and the like. When two or more of these substituents are present, they may be the same or different.

The polymeric magenta coupler which can be used in the present invention includes not only a homopolymer or copolymer of the monomer represented by formula (IV), but also a copolymer obtained from the monomer of formula (IV) and non-color-forming ethylenically unsaturated monomers which do not couple with an oxidation product of an aromatic primary amine developing agent.

Specific examples of the non-color-forming ethylenically unsaturated monomer to be copolymerized with the monomer of formula (IV) are acrylic esters, e.g., methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, acetoxyethyl acrylate, phenyl acrylate, 2-methoxy acrylate, 2-ethoxy acrylate, 2-(2-methoxyethoxy)ethyl acrylate, etc.; methacrylic esters, e.g., methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, cyclohexyl methacrylate, 2-hydroxyethyl methacrylate, 2-ethoxyethyl methacrylate, etc.; crotonic esters, e.g., butyl crotonate, hexyl crotonate, etc.; vinyl esters, e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl methoxyacetate, vinyl benzoate, etc.; maleic diesters, e.g., diethyl maleate, dimethyl maleate, dibutyl maleate, etc.; fumaric esters, e.g., diethyl fumarate, dimethyl furamate, dibutyl fumarate, etc.; itaconic esters, e.g., diethyl itaconate, dimethyl itaconate, dibutyl itaconate, etc.; acrylamides, e.g., acrylamide, methylacrylamide, ethylacrylamide, propylacrylamide, n-butylacrylamide, t-butylacrylamide, cyclohexylacrylamide, 2-methoxyethylacrylamide, dimethylacrylamide, diethylacrylamide, phenylacrylamide, etc.; methacrylamides, e.g., methylmethacrylamide, ethylmethacrylamide, n-butylmethacrylamide, t-butylmethacrylamide, 2-methoxymethacrylamide, dimethylmethacrylamide, diethylmethacrylamide, etc.; vinyl ethers, e.g., methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, methoxyethyl vinyl ether, dimethylaminoethyl vinyl ether, etc.; styrenes, e.g., styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, isopropylstyrene, butylstyrene, chloromethylstyrene, methoxystyrene. butoxystyrene, acetoxystyrene, dichlorostyrene, chlorostyrene, bromostyrene, methyl vinylbenzoate, 2-methylstyrene, etc.; and the like.

Examples of other comonomers to be copolymerized with the monomer of formula (IV) include allyl compounds (e.g., allyl acetate, etc.), vinyl ketones (e.g., methyl vinyl ketone, etc.), vinyl heterocyclic compounds (e.g., vinylpyridine, etc.), glycidyl esters (e.g., glycidyl acrylate, etc.), unsaturated nitriles (e.g., acrylonitrile, etc.), acrylic acid, methacrylic acid, itaconic acid, maleic acid, itaconic acid monoalkyl esters (e.g., monomethyl itaconate, etc.), maleic acid monoalkyl esters (e.g., monomethyl maleate, etc.), citraconic acid, vinylsulfonic acid, acryloyloxyalkylsulfonic acids (e.g., acryloyloxymethylsulfonic acid, etc.), acrylamidoalkylsulfonic acids (e.g., 2-acrylamido-2-methylethanesulfonic acid, etc.), and so on. The acids of the above-enumerated compounds may be in the form of a salt with an alkali metal (e.g., sodium, potassium, etc.) or an ammonium ion.

Preferred among these comonomers are acrylic esters, methacrylic esters, styrenes, maleic esters, acrylamides, and methacrylamides. These comonomers may be used either individually or in combinations of two or more thereof. For example, a combination of n-butyl acrylate and styrene and a combination of n-butyl acrylate and butylstyrene, t-butylmethacrylamide and n-butyl acrylate can be employed.

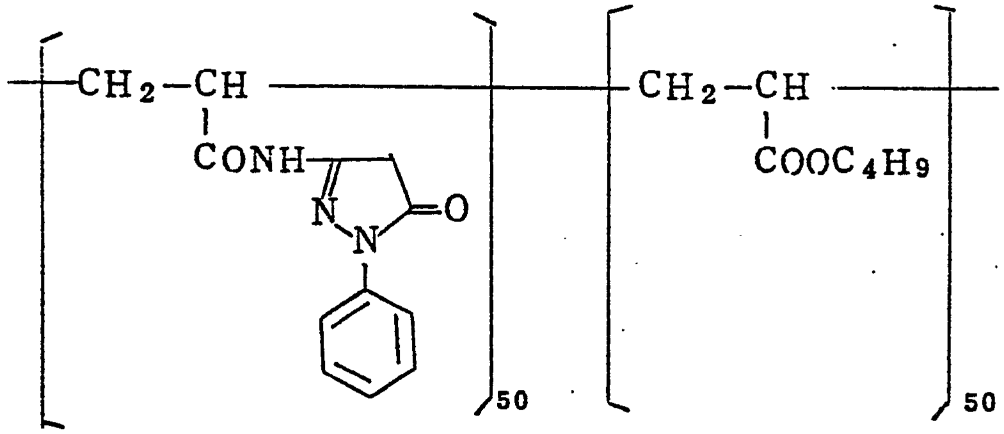
The above-described polymeric magenta couplers usually contain the monomer unit derived from the compound of formula (IV) in a proportion of from 5 to 80% by weight, and preferably from 30 to 70% by weight in view of color reproducibility, color developability, and stability. These polymeric magenta couplers usually have an equivalent molecular weight (grams of polymer containing 1 mol of a monomer coupler) of about 250 to 4,000, though not limiting.

The polymeric couplers according to the present invention are added to a silver halide emulsion layer or layers adjacent thereto. When added to a silver halide emulsion layer, the amount of the polymeric magenta coupler to be used ranges from 0.005 to 0.5 mol, and preferably from 0.01 to 0.10 mol, per mol of silver. When added to a light-insensitive layer, the amount to be used ranges from 0.01 to 1.0 g, and preferably from 0.1 to 0.5 g, per m^2.

The polymeric magenta couplers can be prepared in the same manner as described for polymeric cyan couplers using the processes of U.S. Patents 3,451,820, 4,080,211, and 3,370,952, etc. In particular, the above-described polymeric magenta couplers can be synthesized by using polymerization initiators and solvents disclosed in Japanese Patent Application (OPI) Nos. 5543/81, 94752/82, 176038/82, 204038/82, 28745/83, 10738/83, 42044/83, and 145944/83. The polymerization temperature should be determined in connection with the desired molecular weight of the resulting polymer, the kind of the polymerization initiator to be used, or like factors can be selected from a wide range of from 0°C or less up to 100°C or more, and usually of from 30°C to 100°C.

Specific but non-limiting examples of the polymeric magenta couplers which can be used in the present invention are shown below.

(P-1)



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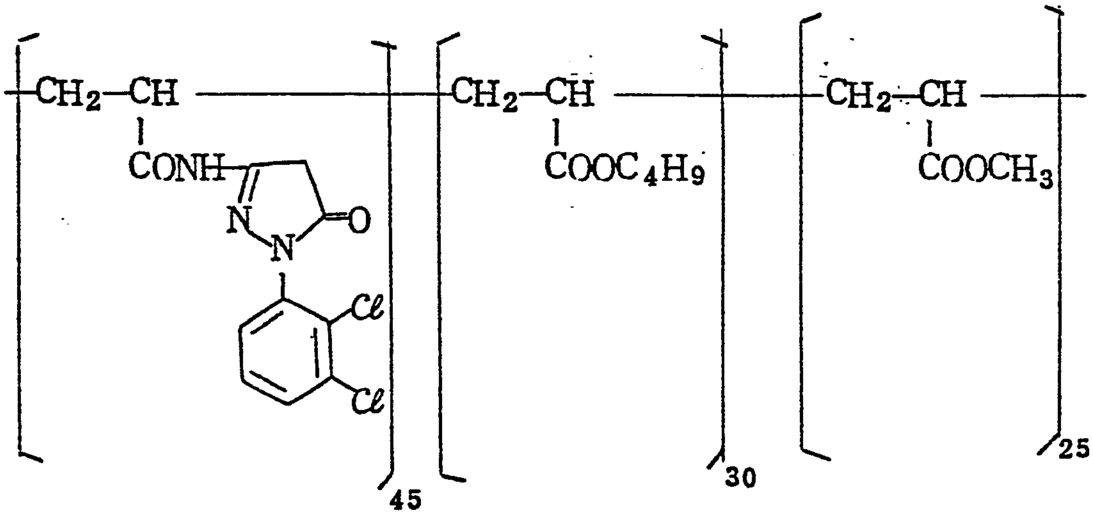

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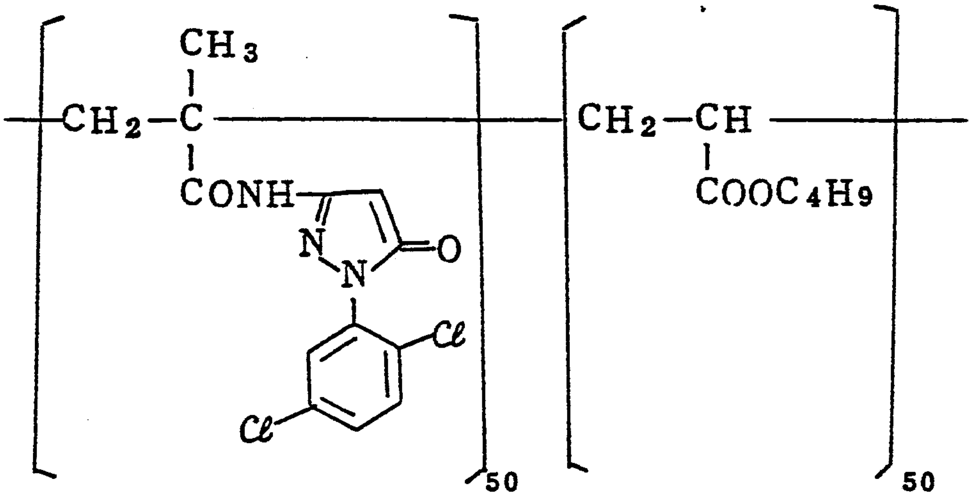

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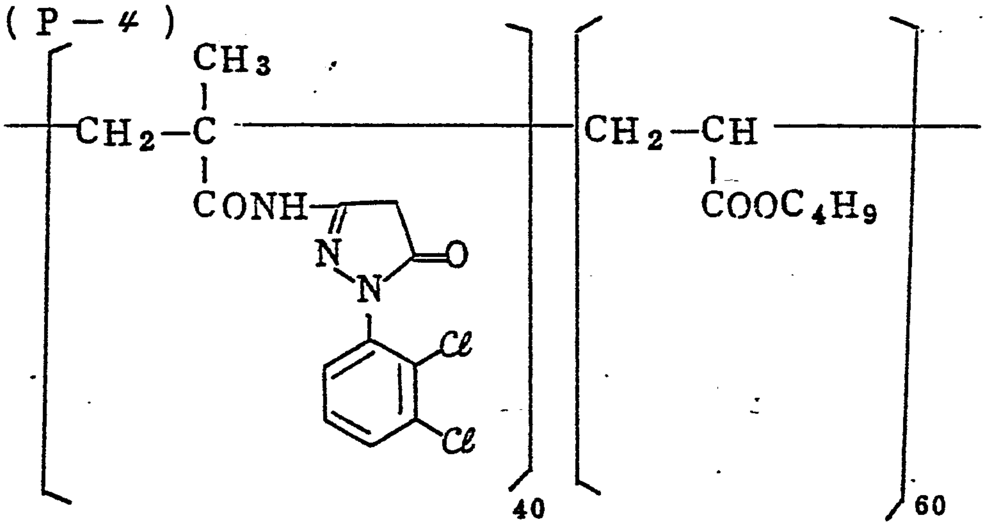

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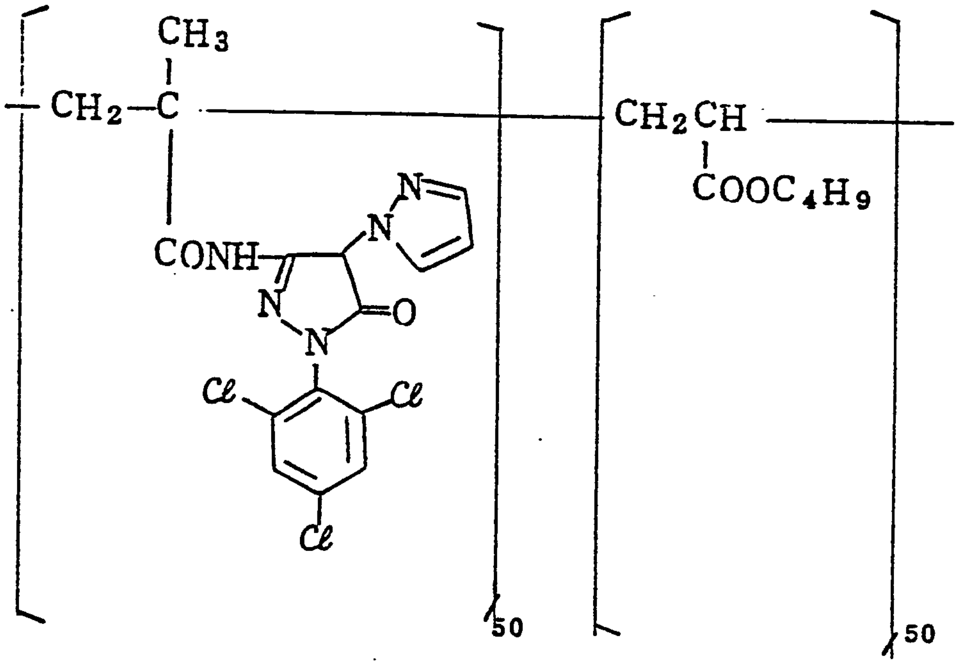
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Cl
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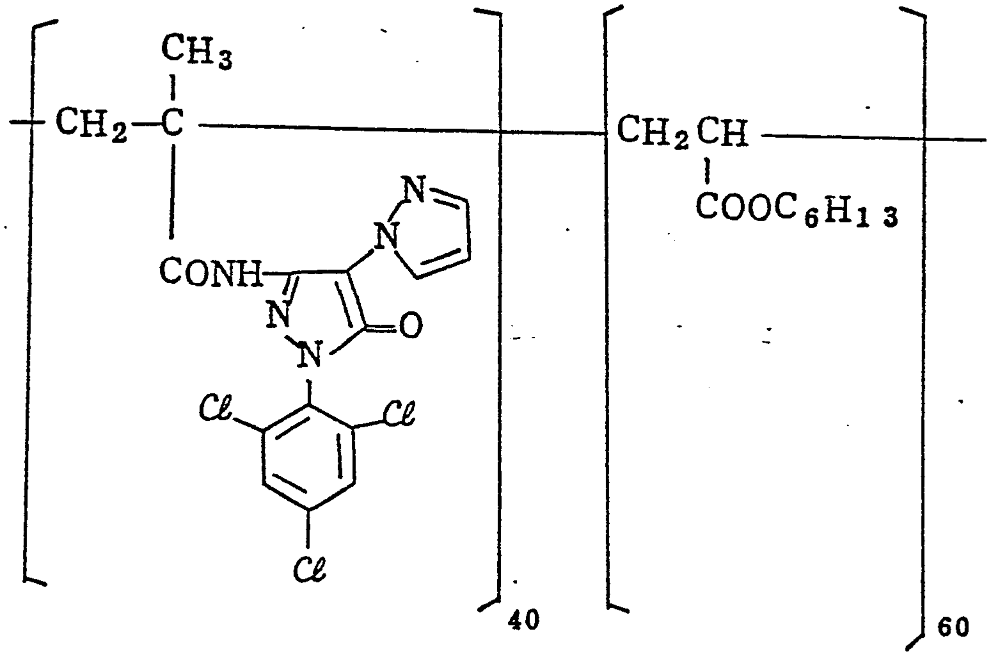
(P-6)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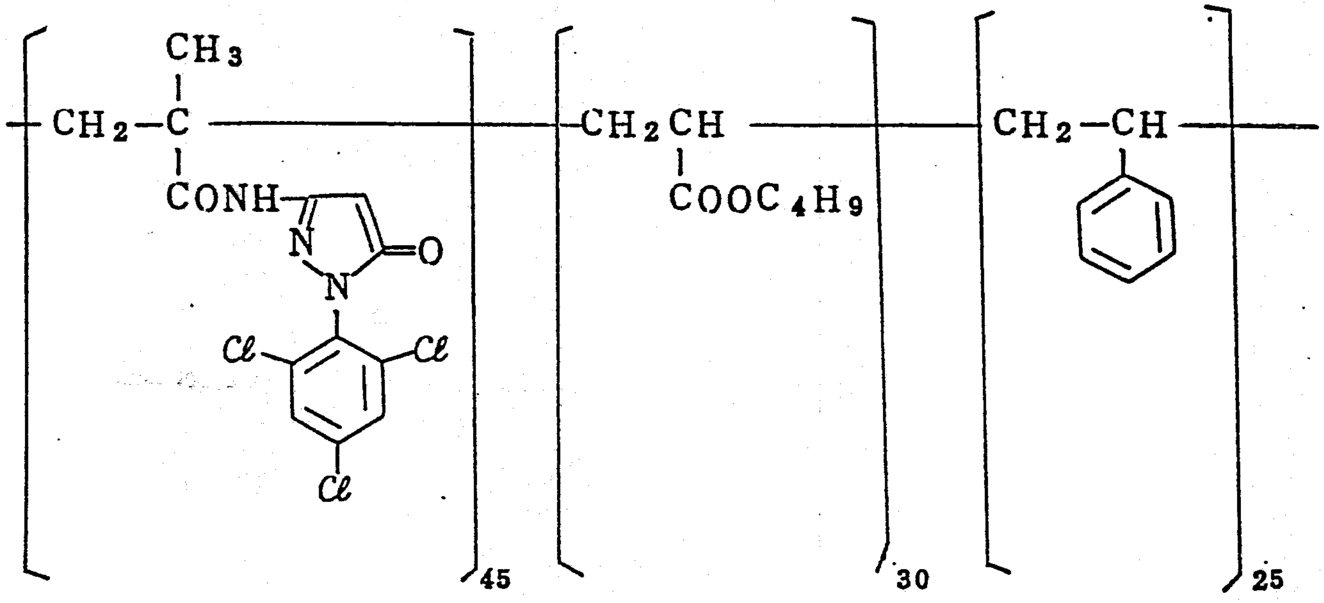
(P－7)



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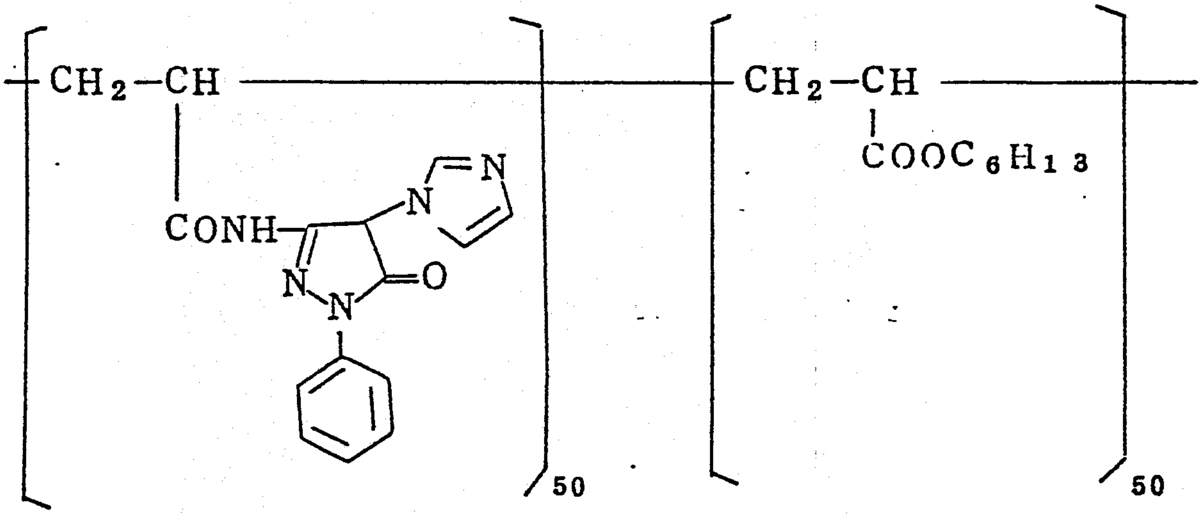

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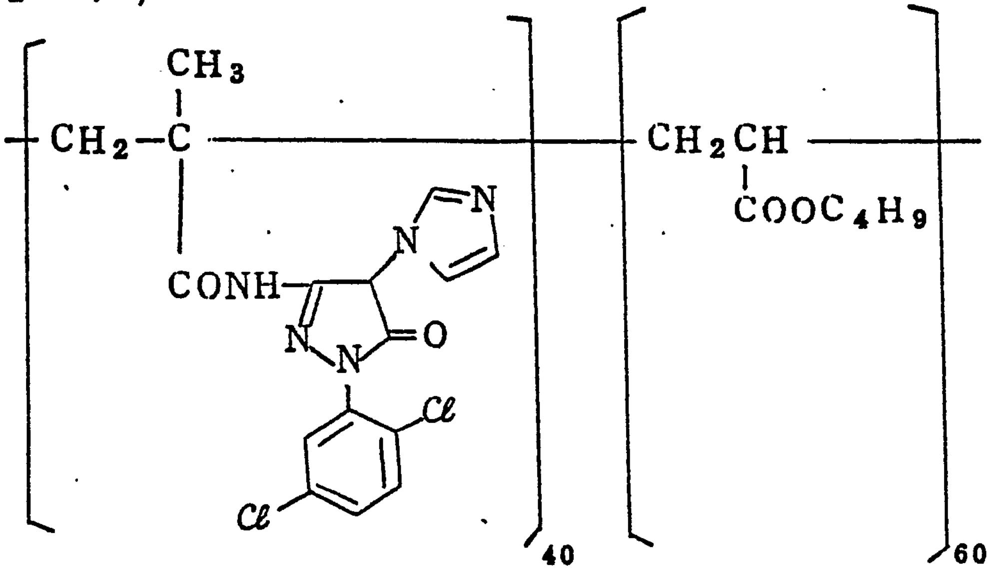
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N
O
Cl
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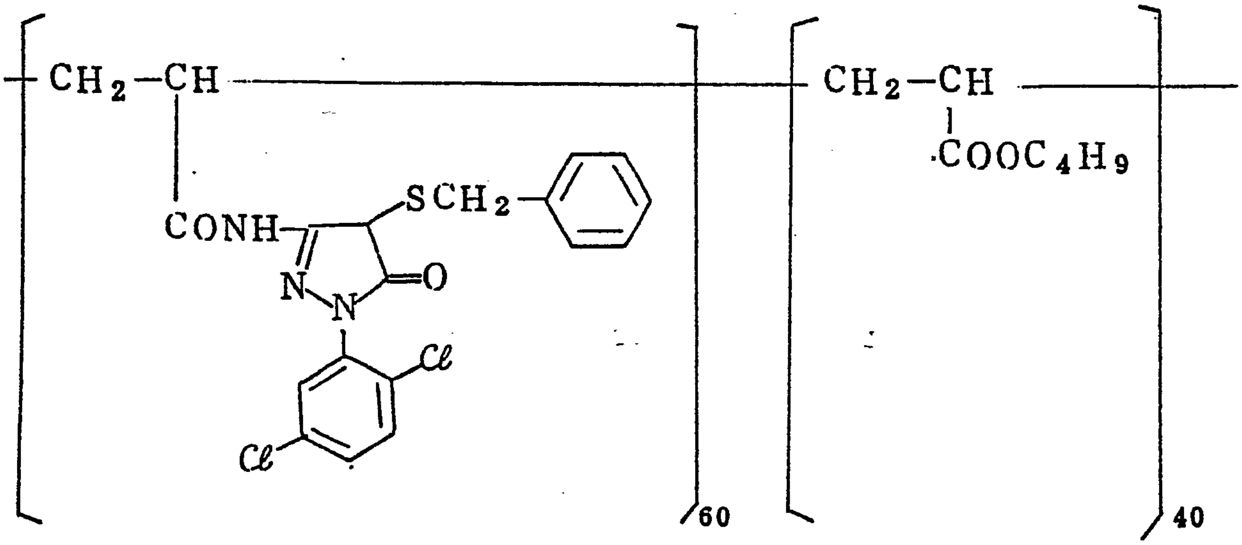
60

(P-10)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CONH
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O
Cl
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CH2
CH
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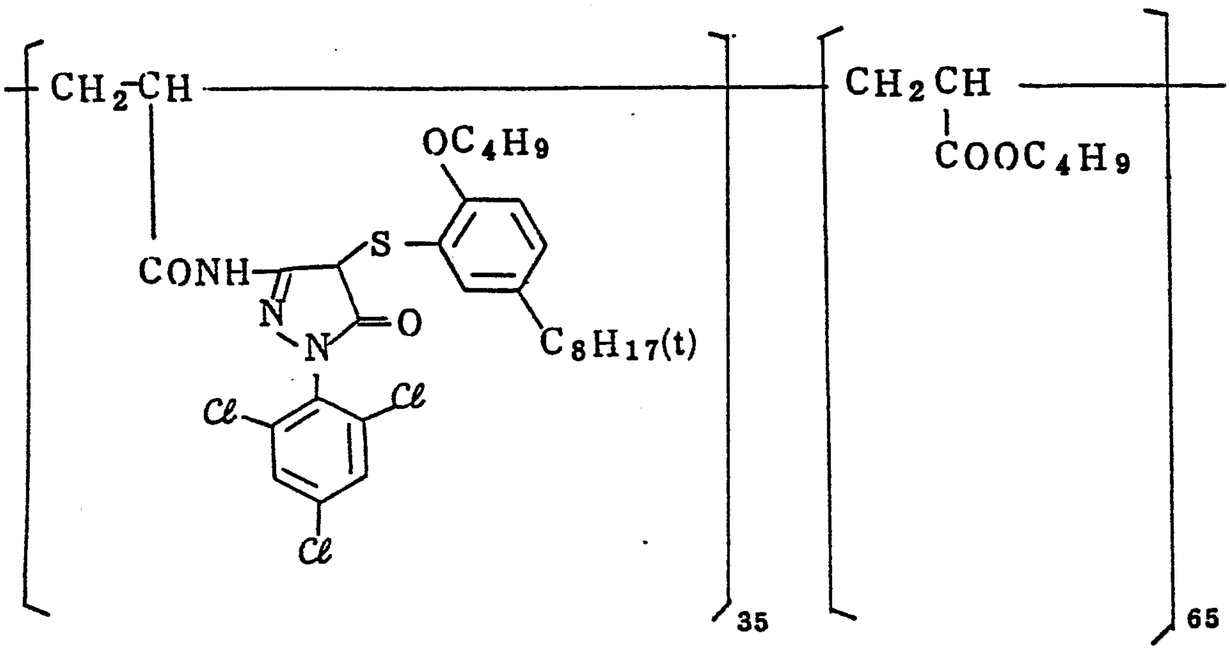
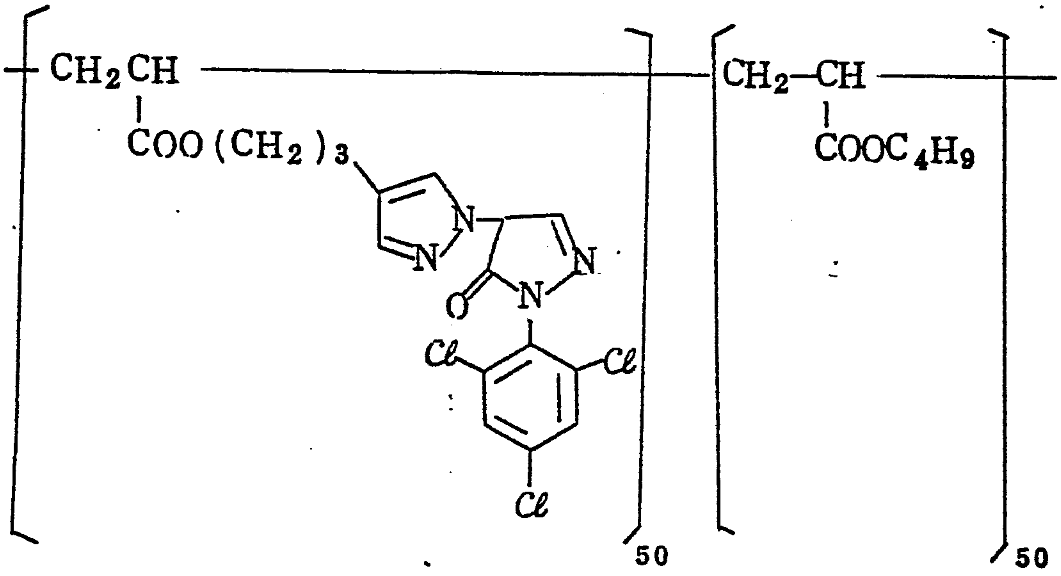
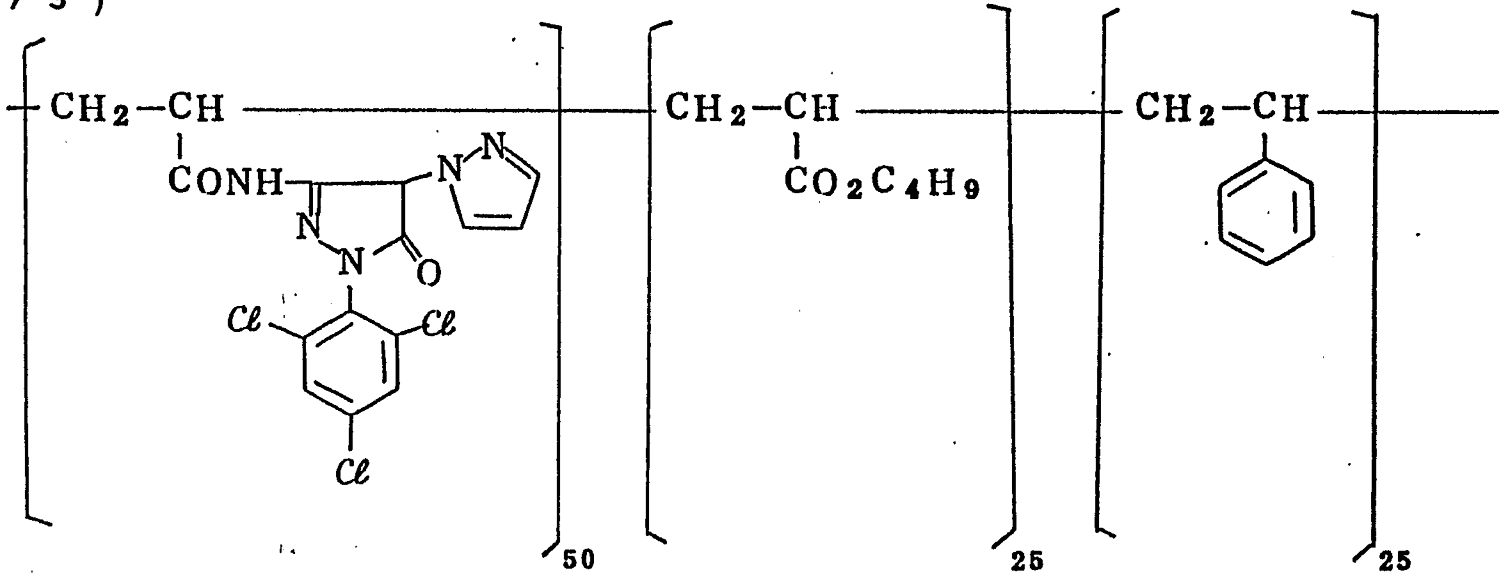
(P－11)



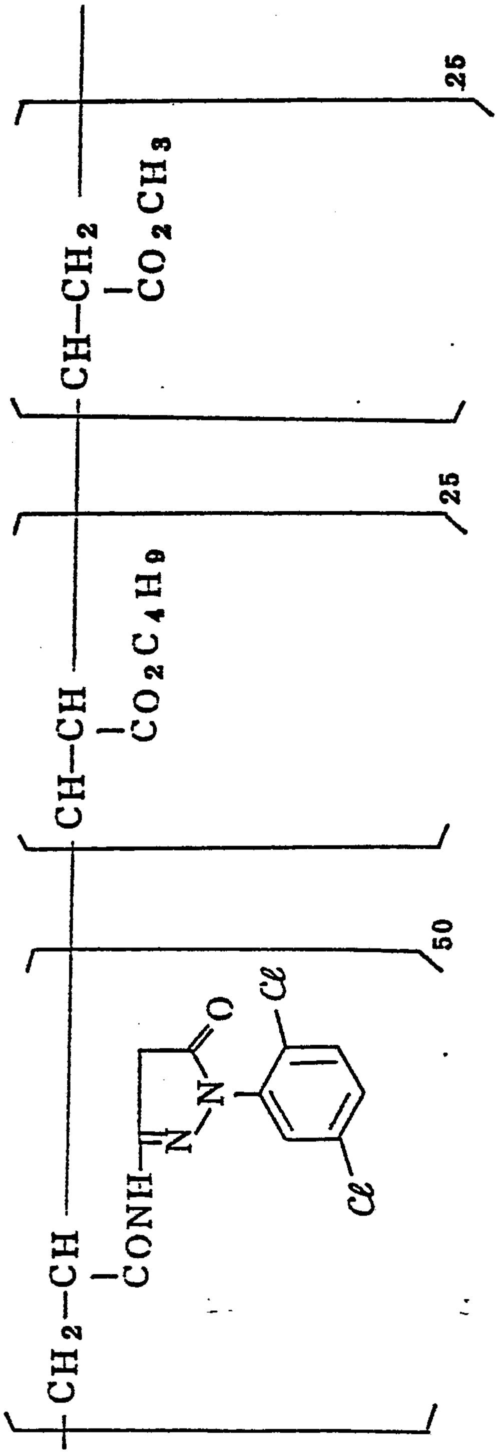
(P－12)



(P – 13)



(P — 14)



Silver halide which can be used in the photographic emulsion layer of the photographic material of the present invention may be any of silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide, and silver chloride. Preferred are silver iodobromide and silver iodochlorobromide having a silver iodide content of not more than about 30 mol%, and more preferred is silver iodobromide having a silver iodide content of from about 2 to about 25 mol%.

The silver halide grains in the photographic emulsion may have a regular crystal form, such as cubic, octahedral and tetradecahedral forms, an irregular crystal form, such as a spherical form, a crystal form having a defect, such as a twin, or a composite crystal form thereof.

The silver halide may be fine grains having a grain size of about 0.1 µm or smaller or giant grains having a projected area diameter reaching about 10 µm. The silver halide emulsion may be a mono-dispersion having narrow size distribution or a poly-dispersion having broad size distribution.

The silver halide emulsions to be used can be prepared by known processes as disclosed, e.g., in Research Disclosure, No. 17643, pp.22-23, "I. Emulsion Preparation and Types" (Dec., 1978), ibid, No. 18716, p.648 (Nov., 1979), P. Glafkides, Chimie et Physique Photographique, Paul Montel (1967), G.F. Duffin, Photographic Emulsion Chemistry, Focal Press (1966); V.L. Zelikman et al., Making and Coating Photographic Emulsion, Focal Press (1964), etc. In some detail, the emulsion can be prepared by any of the acid process, the neutral process, the ammonia process, etc. The reaction between a soluble silver salt and a soluble halogen salt can be carried out by any of a single jet process, a double jet process, a combination thereof, and the like. A so-called reverse mixing process in which grains are formed in the presence of excess silver ions may be used. Further, a so-called controlled double jet process, in which a pAg value of a liquid phase in which silver halide grains are formed is maintained constant, may also be used. According to the controlled double jet process, a silver halide emulsion having a regular crystal form and a substantially uniform grain size can be obtained. Two or more silver halide emulsions separately prepared may be used as a mixture.

The silver halide emulsion comprising grains having a regular crystal form (regular grains) can be prepared by controlling pAg and pH values during grain formation. For details, reference can be made to, e.g., Photographic Science and Engineering, Vol. 6, pp.159-165 (1962); Journal of Photographic Science, Vol. 12, pp. 242-251 (1964), U.S. Patent 3,655,394, and British Patent 1,413,748.

The monodisperse emulsion as above referred to typically includes those containing silver halide grains having a mean grain size of about 0.1 µm or greater, and particularly of from about 0.25 to 2 µm, in which at least about 95% by weight or number of the total grains fall within a size range of 40%, and particularly 20%, of the mean grain size. Such monodisperse emulsions can be prepared by the processes described in U.S. Patents 3,574,628 and 3,655,394, and British Patent 1,413,748. The monodisperse emulsions described in Japanese Patent Application (OPI) Nos. 8600/73, 39027/76, 83097/76, 137133/78, 48521/79, 99419/79, 37635/83, and 49938/83, etc. can also be used to advantage in the present invention.

Plate-like (tabular) grains having an aspect ratio of about 5 or more (i.e., 5/1 or more) can also be used. Such plate-like grains can be prepared easily by the processes described in Gutoff, Photographic Science and Engineering, Vol. 14, pp.248-257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048, and 4,439,520, British Patent 2,112,157, etc. Use of the plate-like grains brings about improvements on efficiency of color sensitization by sensitizing dyes, graininess, sharpness, and the like, as suggested in U.S. Patent 4,434,226.

The individual silver halide crystals may have either a homogeneous structure or a heterogeneous structure, such as a core-shell structure or a layered structure differing in halogen composition. These emulsion grains are disclosed in British Patent 1,027,146, U.S. Patents 3,505,068 and 4,444,877, Japanese Patent Application No. 248469/83, etc. Further, they may have a heterogeneous structure in which a silver halide grain having a different halogen composition or a compound other than silver halides, e.g., silver thiocyanate, lead oxide, etc., is fused by epitaxy. These emulsion grains are disclosed 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, Japanese Patent Application (OPI) No. 162540/84, etc.

A mixture of silver halide grains having various crystal forms can also be employed.

The emulsion to be used in the present invention is usually subjected to physical ripening, chemical ripening and spectral sensitization. Additives to be used in these steps and other photographically useful additives which can be used in the present invention are described in Research Disclosure (RD), No. 17643 (Dec. 1978) and ibid, No. 18716 (Nov. 1979) as tabulated below.

Photographic Additives

Kind	RD17643	RD18716
Chemical sensitizer	p.23	p.648 right column (RC)
Sensitivity increasing agent		do.
Spectral sensitizer and supersensitizer	pp.23-24	p.648 RC-p.649 RC
Brightening agent	p.24	
Antifoggant and stabilizer	pp.24-25	p.649 RC
Light absorbent, filter dye, and ultraviolet absorbent	pp.25-26	p.649 RC-p.650 left column (LC)
Stain inhibitor	p.25 RC	p.650 LC-RC
Dye image stabilizer	p.25	
Hardener	p.26	p.651 RC
Binder	p.26	do.
Plasticizer and lubricant	p.27	p.650 RC
Coating aid and surface active agent	pp.26-27	do.
Antistatic	p.27	do.

In addition to the foregoing cyan and magenta couplers, other various color couplers can be used in this invention. Specific examples of usable color couplers are described in Research Disclosure, No. 17643, VII-C to G. Important are dye forming couplers which produce three primary colors according to subtractive color process, i.e., yellow, magenta, and cyan. In this connection, anti-diffusible 4-or 2-equivalent couplers which can be used advantageously include those described in Research Disclosure, No. 17643, VII-C to D and, in addition, couplers hereinafter described.

Yellow couplers to be used typically include hydrophobic acylacetamide couplers having a ballast group, whose specific examples are given in U.S. Patents 2,407,210, 2,875,057, and 3,265,506. In the present invention, 2-equivalent yellow couplers are preferred. Typical examples of such couplers are those of oxygen-release type as described in U.S. Patents 3,408,194, 3,447,928, 3,933,501, and 4,022,620; and those of nitrogen-release type as described in Japanese Patent Publication No. 10739/83, U.S. Patents 4,401,752 and 4,326,024, Research Disclosure , No. 18053 (Apr., 1979), British Patent 1,425,020, and West German Patent Publication Nos. 2,219,917, 2,261,361, 2,329,587, and 2,433,812. Inter alia, α-pivaloylacetanilide couplers are excellent in color fastness, and particularly fast ness to light, and α-benzoylacetanilide couplers provide high color densities.

The magenta couplers which can be used in the present invention include indazolone or cyanoacetyl couplers, and preferably 5-pyrazolone or pyrazoloazole couplers which have a ballast group and are thereby hydrophobic. The 5-pyrazolone couplers preferably have an arylamino group or an acylamino group at the 3-position from the standpoint of hue and density of the developed color. Typical examples of such couplers are described, e.g., in U.S. Patents 2,311,082, 2,343,703, 2,600,788, 2,908,573, 3,062,653, 3,152,896, and 3,936,015. Preferred releasable groups for 2-equivalent 5-pyrazolone couplers are nitrogen atom-release type groups as described in U.S. Patent 4,310,619 and arylthio groups as described in U.S. Patent 4,351,897. 5-Pyrazolone couplers having the ballast group described in European Patent 73,636 provide high color densities. The pyrazoloazole couplers include pyrazolobenzimidazoles described in U.S. Patent 3,061,432, and preferably pyrazolo[5,1-c][1,2,4]triazoles described in U.S. Patent 3,725,067, pyrazolotetrazoles described in Research Disclosure, No. 24220 (June, 1984) and Japanese Patent Application (OP) No. 33552/85, and pyrazolopyrazoles described in Research Disclosure, No. 24230 (Jun., 1984) and Japanese Patent Application (OPI) No. 43659/85. From the standpoint of reduced side absorption of yellow and light-fastness of the produced dye, the imidazolo[1,2-b]pyrazoles described in U.S. Patent 4,500,630 are preferred, and the pyrazolo[1,5-b][1,2,4]triazoles described in U.S. Patent 4,540,654 are particularly preferred.

Cyan couplers which can be used in the present invention include hydrophobic and anti-diffusible naphthoic and phenolic couplers. Typical examples are naphthol couplers described in U.S. Patent 2,474,293, and preferably 2-equivalent naphthol couplers of oxygen-release type described in U.S. Patents 4,052,212, 4,146,396, 4,228,233, and 4,296,200. Examples of the phenolic couplers are described in U.S. Patents 2,369,929, 2,801,171, 2,772,162, and 2,895,826.

Cyan couplers which form cyan dyes fast to moisture and heat are advantageously used in the present invention. Typical examples of such cyan couplers include phenolic couplers having an alkyl group having at least 2 carbon atoms at the m-position as described in U.S. Patent 3,772,002; 2,5-diacylamino-substituted phenol couplers as described in U.S. Patents 2,772,162, 3,758,308, 4,126,396, 4,334,011, and 4,327,173, West German Patent Publication No. 3,329,729, and European Patent 121,365; phenolic couplers having a phenylureido group at the 2-position and an acylamino group at the 5-position as described in U.S. Patents 3,446,622, 4,333,999, 4,451,559, and 4,427,767; and the like.

In order to correct unnecessary absorptions of the developed color, it is preferable to use a colored coupler in combination for masking in color light-senisitive materials for photogrpahing. Typical examples of the colored couplers are yellow-colored magenta couplers described in U.S. Patent 4,163,670 and Japanese Patent Publication No. 39413/82 and magenta-colored cyan couplers described in U.S. Patents 4,004,929 and 4,138,258 and British Patent 1,146,368. Other examples of colored couplers are described in Research Disclosure, No. 17643, VII-G (Dec. 1978).

Graininess can be improved by using a coupler which forms a dye having moderate diffusibility. Examples of such a coupler are described in U.S. Patent 4,366,237 and British Patent 2,125,570 for magenta couplers; and in European Patent 96,570 and West German Patent Publication No. 3,234,533 for yellow, magenta, and cyan couplers.

The dye forming couplers and the above-described special couplers may be in the form of a polymer including a dimer. Typical examples of polymerized dye forming couplers are described in U.S. Patents 3,451,820 and 4,080,211. Typical examples of polymerized magenta couplers are described in British Patent 2,102,173 and U.S. Patent 4,367,282.

Couplers capable of releasing a photographically useful residue upon coupling can also be used in this invention with advantage. Useful examples of DIR couplers which release a developing inhibitor are described in Research Disclosure, No.17643, VII-F (Dec. 1978).

DIR (development inhibitor releasing) couplers which are preferably combined with the present invention include those which are inactivated in a developer as described in Japanese Patent Application (OPI) No. 151944/82; timing type DIR couplers as described in U.S. Patent 4,248,962 and Japanese Patent Application (OPI) No. 154234/82; and reactive type DIR couplers as described in Japanese Patent Application (OPI) No. 39653/84. Particularly preferred are developer-inactivated type DIR couplers described in Japanese Patent Application (OPI) Nos. 151944/82 and 217932/83 and Japanese Patent Application Nos. 75474/84, 82214/84, and 90438/84; and reactive type DIR couplers described in Japanese Patent Application No. 39653/84.

The light-sensitive materials of the present invention can also use couplers which imagewise release a nucleating agent or a development accelerator or a precursor thereof at the time of development. Specific examples of these couplers are described in British Patents 2,097,140 and 2,131,188. Couplers capable of releasing a nucleating agent having adsorptivity onto silver halide, such as those described in Japanese Patent Application (OPI) Nos. 157638/84 and 170840/84, are particularly preferred.

Supports which can be used suitably in the present invention are described, e.g., in Research Disclosure, No. 17643, p.28 (Dec. 1987) and ibid, No.18716, p. 647, right column to p. 648, left column (Nov. 1979).

The color photographic material in accordance with the present invention can be subjected to development processing by known methods as described, e.g., in Research Disclosure, No. 17643, pp.28-29 (Dec. 1978) ibid, No. 18716, p. 651, left to right columns (Nov.1979).

Color developing solutions to be used for development processing preferably include alkaline aqueous solutions containing, as a main component, an aromatic primary amine developing agent. Usable color developing agents include aminophenol compounds, and preferably p-phenylenediamine compounds. Typical examples of the latter are 3-methyl-4-amino-N,N-di ethylaniline, 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 sulfates, hydrochlorides or p-toluenesulfonates thereof. These diamines are more stable and thereby preferred in the form of a salt rather than in a free form.

The color developing solutions generally contain pH buffers, such as carbonates, borates or phosphates of alkali metals, and developing inhibitors or antifoggants, such as bromides, iodides, benzimidazoles, benzothiazoles, mercapto compounds, etc. If desired, the color developing solutions may further contain preservatives, e.g., hydroxylamines, sulfites, etc.; organic solvents, e.g., triethanolamine, diethylene glycol, etc.; development accelerators, e.g., benzyl alcohol, polyethylene glycol, quaternary ammonium salts, amines, etc.; competing couplers; nucleating agents, e.g., sodium boron hydride, etc.; auxiliary developing agents, e.g., 1-phenyl-3-pyrazolidone, etc.; tackifiers; various chelating agents, e.g., aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids, phosphonocarboxylic acids, etc.; antioxidants, e.g., those described in West German Patent Publication No. 2,622,950; and the like.

Reversal color light-sensitive materials are usually subjected to black-and-white development and then to color development. Black-and-white developing solutions to be used can contain one or more of known black-and-white developing agents, such as dihydroxybenzenes (e.g., hydroquinone), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone) and aminophenols (e.g., N-methyl-p-aminophenol).

The photographic emulsion layers after color development are usually subjected to bleaching. Bleaching may be effected simultaneously with fixation, or these two steps may be carried out separately. For speeding up of processing, bleaching may be followed by bleach-fixation (blix). Bleaching agents to be used in bleaching or blix include compounds of polyvalent metals, e.g., iron (III), cobalt (III), chromium (VI), copper (II), etc., peracids, quinones, nitroso compounds, and the like. Examples of these bleaching agents are ferricyanides; bichromates; organic complex salts of iron (III) or cobalt (III), such as complex salts with aminopolycarboxylic acids, e.g., ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, 1,3-diamino-2-propanoltetraacetic acid, etc., or organic acids, e.g., citric acid, tartaric acid, malic acid, etc.; persulfates; manganates; nitrosophenol; and so on. Of these, (ethylenediaminetetraacetato)iron (III) salts, (diethylenetriaminepentaacetato)iron (III) salts and persulfates are preferred in view of speeding up of processing and conservation of the environment. In particular, (ethylenediaminetetraacetato)iron (III) salts are useful in both of an independent bleaching bath and a bleach-fix monobath.

The bleaching bath, bleach-fix bath or a pre-bath thereof can contain, if desired, a bleaching accelerator. Examples of useful bleaching accelerators are compounds having a mercapto group or a disulfide group as described in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, Japanese Patent Application (OPI) Nos. 32736/78, 57831/78, 37418/78, 65732/78, 72623/78, 95630/78, 95631/78, 104232/78, 124424/78, 141623/78 and 28426/78, Research Disclosure, No. 17129 (July 1978); thiazolidine derivatives as described in Japanese Patent Application (OPI) No. 140129/75; thiourea derivatives as described in Japanese Patent Publication No. 8506/70, Japanese Patent Application (OPI) Nos. 20832/77 and 32735/78, and U.S. Patent 3,706,561; iodides as described in West German Patent 1,127,715 and Japanese Patent Application (OPI) No. 16235/83; polyethylene oxides as described in West German Patents 966,410 and 2,748,430; polyamine compounds as described in Japanese Patent Publication No. 8836/70; the compoudns described in Japanese Patent Application (OPI) Nos. 42434/84, 59644/74, 94927/78, 35727/79, 26506/80, and 163940/83; and iodine or bromine ions. Preferred among them are compoudns having a mercapto group or a disulfide group because of their great acceleratory effects. In particular, the compounds disclosed in U.S. Patent 3,893,858, West German Patent 1,290,812 and Japanese Patent Application (OPI) No. 95630/78 are preferred. The compounds disclosed in U.S. Patent 4,552,834 are also preferred. These bleaching accelerators may be incorporated into the light-sensitive material. These bleaching accelerators are particularly effective for bleach-fix of color light-sensitive materials for photography.

Fixing agents to be used for fixation include thiosulfates, thiocyanates, thioethers, thioureas, and a large amount of iodides, with thiosulfates being commonly employed. Sulfites, bisulfites or carbonylbisulfite addition compounds are suitably used as preservatives of the bleach-fix bath or fixing bath.

The bleach-fix or fixation is usually followed by washing and/or stabilization. Washing and stabilizing solutions may contain various known compounds for the purpose of preventing precipitation or saving water. For example, additives to be used for prevention of precipitation include water softeners, such as inorganic phosphoric acids, aminopolycarboxylic acids, organic aminopolyphosphonic acids, organic phosphoric acids, etc.; bactericides or fungicides; and metal salts, such as magnesium salts, aluminum salts and bismuth salts. Surface active agents and various hardeners can also be added for the purpose of reducing a drying load or preventing uneven drying. The compounds described in L.E. West, Photo. Sci. Eng., Vol. 6, pp.344-359 (1965) may also be used. In particular, addition of chelating agents and fungicides is effective.

Washing is generally carried out by using two or more washing vessels arranged countercurrently, by which water saving can be effected. The washing step may be replaced by a multi-stage countercurrent stabilization step as described in Japanese Patent Application (OPI) No. 8543/82, in which 2 to 9 vessels arranged countercurrently are required. The stabilization baths to be used in this step contain various compounds for image stabilization in addition to the aforesaid additives. Such compounds include various buffers for film pH adjustment (e.g., to a pH of from 3 to 9) (e.g., borates, metaborates, borax, phosphonates, carbonates, potassium hydroxide, sodium hydroxide, aqueous ammonia, monocarboxylic acids, dicarboxylic acids, polycarboxylic acids and combinations thereof) and aldehydes, e.g., formalin. If desired, the stabilization bath may further contain other additives, such as chelating agents (e.g., inorganic phosphoric acids, aminopolycarboxylic acids, organic phosphoric acids, aminopolyphosphonic acids, phosphonocarboxylic acids, etc.), bactericides (e.g., benzoisothiazolinone, irithiazolone, 4-thiazolinebenzimidazole, halogenated phenols, sulfanilamide, benzotriazole, etc.), surface active agents, fluorescent brightening agents, hardeners, and the like. These compounds may be added in combinations of two or more thereof for the same or different purposes.

It is preferable to add various ammonium salts to the stabilization bath as film pH adjusting agents after processing. Examples of such ammonium salts are ammonium chloride, ammonium nitrate, ammonium sulfate, ammonium phosphate, ammonium sulfite, ammonium thiosulfate, etc.

For processing of color light-sensitive materials for photographing, the (washing-stabilization) step after fixation that is commonly adopted may be replaced by the aforesaid stabilization step and washing step (water saving processing). In this case, if the magenta coupler used is 2-equivalent, formalin may be excluded from the stabilization bath.

The time required for washing and stabilization varies depending on the type of the light-sensitive material processed and the conditions for processing, and usually ranges from 20 seconds to 10 minutes, and preferably from 20 seconds to 5 minutes.

For the purpose of simplification and speeding up of processing, a color developing agent, preferably in the form of its precursor, can be incorporated into the silver halide color photographic material according to the present invention. The precursors of the color developing agent suitable for incorporation include indoaniline compounds as described in U.S. Patent 3,342,597, Schiff base type compounds as in U.S. Patent 3,342,599, Research Disclosure, No. 14850 (Aug. 1976) and ibid, No. 15159 (Nov. 1976), aldol compounds as in Research Disclosure, No. 13924, metal complexes as in U.S. Patent 3,719,492, urethane compounds as in Japanese Patent Application (OPI) No. 135628/78, as well as various salt types as in Japanese Patent Application (OPI) Nos. 6235/81, 16133/81, 59232/81, 67842/81, 83734/81, 83735/81, 83736/81, 89735/81, 81837/81, 54430/81, 106241/81, 107236/81, 97531/82, and 83565/82, etc.

For the purpose of accelerating color development, the color light-sensitive materials of the present invention can further contain therein various 1-phenyl-3-pyrazolidones. Typical examples thereof are described in Japanese Patent Application (OPI) Nos. 64339/81, 144547/82, 211147/82, 50532/83, 50536/83, 50533/83, 50534/83, 50535/83, and 115438/83, etc.

Each of the above-described processing solutions is used at a temperature between 10°C and 50°C, and usually between 33°C and 38°C. It is possible to use higher temperatures to accelerate processing to thereby reduce the processing time or lower temperatures required to achieve improvements on image quality or stability of processing solutions. In order to save silver used in light-sensitive materials, intensification may be carried out by using a cobalt or hydrogen peroxide intensifier, as described in West German Patent 2,226,770 or U.S. Patent 3,674,499.

If necessary, each of the processing baths may be provided with a heater, a temperature sensor, a liquid level sensor, a circulating pump, a filter, a floating lid, a squeegee, etc.

In cases where processing is carried out in a continuous manner, a constant finish can be assured by preventing variations of processing solution compositions by using a replenisher for each processing solution. The amount to be replenished can be reduced to a half or less of the standard amount to cut the cost.

The present invention is now illustrated in greater detail by way of the following examples, but it is to be understood that the present invention is not limited thereto.

EXAMPLE 1

Onto a triacetyl cellulose film support having a subbing layer were coated lst to l5th layers having the following compositions to prepare a multi-layer color light-sensitive material. The meanings of the compound designations set forth below are indicated following the examples. The resulting sample was designated as Sample l0l.

1st Layer (Antihalation Layer):

Black colloidal silver	0.18 g of Ag
Gelatin	1.40 g/m^2

2nd Layer (Intermediate Layer):

2,5-Di-pentadecylhydroquinone	0.18 g/m^2
C-1	0.07 mol/mol of AgX (X: halogen)
U-1	0.08 g/m^2
U-2	0.08 g/m^2
HBS-1	0.10 g/m^2

HBS-2	0.02 g/m^2
Gelatin	1.04 g/m^2

3rd Layer (1st Red-Sensitive Emulsion Layer):

Silver iodobromide emulsion (silver iodide: 6 mol%; mean grain size: 0.8 μm)	0.50 g of Ag
Sensitizing Dye IX	6.9x10^{-5} mol/mol-AgX
Sensitizing Dye II	1.8x10^{-5} mol/mol-AgX
Sensitizing Dye III	3.1x10^{-4} mol/mol-AgX
Sensitizing Dye IV	4.0x10^{-5} mol/mol-AgX
I-13	0.146 mol/mol-AgX
C-4	0.0050 mol/mol-AgX
Gelatin	1.20 g/m^2

4th Layer (2nd Red-Sensitive Emulsion Layer):

Silver iodobromide emulsion (silver iodide: 5 mol%; mean grain size: 0.85 μm)	1.15 g of Ag
Sensitizing Dye IX	5.1x10^{-5} mol/mol-AgX
Sensitizing Dye II	1.4x10^{-5} mol/mol-AgX
Sensitizing Dye III	2.3x10^{-4} mol/mol-AgX
Sensitizing Dye IX	3.0x10^{-5} mol/mol-agX
I-13	0.060 mol/mol-AgX
C-3	0.008 mol/mol-AgX
C-4	0.004 mol/mol-AgX
Gelatin	1.50 g/m^2

5th Layer (3rd Red-Sensitive Emulsion Layer):

Silver iodobromide emulsion (silver iodide: 10 mol%; mean grain size: 1.5 μm)	1.50 g of Ag
Sensitizing Dye IX	5.4×10^{-5} mol/mol-AgX
Sensitizing Dye II	1.4×10^{-5} mol/mol-AgX
Sensitizing Dye III	2.4×10^{-4} mol/mol-AgX
Sensitizing Dye IV	3.1×10^{-5} mol/mol-AgX
C-5	0.018 mol/mol-AgX
C-3	0.003 mol/mol-AgX
C-4	0.0005 mol/mol-AgX
HBS-1	0.32 g/m^2
Gelatin	1.63 g/m^2

6th Layer (Intermiate Layer):

Gelatin	1.06 g/m^2

7th Layer (1st Green-Sensitive Emulsion Layer):

Silver iodobromide emulsion (silver iodide: 6 mol%; mean grain size: 0.8 μm)	0.35 g of Ag
Sensitizing Dye V	3.0×10^{-5} mol/mol-AgX
Sensitizing Dye VI	1.0×10^{-4} mol/mol-AgX
Sensitizing Dye VII	3.8×10^{-4} mol/mol-AgX
C-6	0.120 mol/mol-AgX
C-1	0.021 mol/mol-AgX
C-7	0.030 mol/mol-AgX
C-8	0.025 mol/mol-AgX
HBS-1	0.20 g/m^2

Gelatin	0.70 g/m^2

8th Layer (2nd Green-Sensitive Emulsion Layer):

Silver iodobromide emulsion (silver iodide: 5 mol%; mean grain size: 0.85 μm)	0.75 g of Ag
Sensitizing Dye V	2.1×10^{-5} mol/mol-AgX
Sensitizing Dye VI	7.0×10^{-5} mol/mol-AgX
Sensitizing Dye VII	2.6×10^{-4} mol/mol-AgX
C-6	0.021 mol/mol-AgX
C-8	0.004 mol/mol-AgX
C-1	0.002 mol/mol-AgX
C-7	0.003 mol/mol-AgX
HBS-1	0.15 g/m^2
Gelatin	0.80 g/m^2

9th Layer (3rd Green-Sensitive Emulsion Layer):

Silver iodobromide emulsion (silver iodide: 10 mol%; mean grain size: 1.5 μm)	1.80 g of Ag
Sensitizing Dye V	3.5×10^{-5} mol/mol-AgX
Sensitizing Dye VI	8.0×10^{-5} mol/mol-AgX
Sensitizing Dye VII	3.0×10^{-4} mol/mol-AgX
C-9	0.011 mol/mol-AgX
C-1	0.001 mol/mol-AgX
HBS-2	0.69 g/m^2
Gelatin	1.74 g/m^2

10th Layer (Yellow Filter Layer):

Yellow colloidal silver	0.05 g of Ag

2,5-Di-t-pentadecylhydroquinone	0.03 g/m^2
Gelatin	0.95 g/m^2

11th Layer (1st Blue-Sensitive Emulsion Layer):

Silver iodobromide emulsion (silver iodide: 6 mol%; mean grain size: 0.6 μm)	0.24 g of Ag
Sensitizing Dye VIII	3.5x10^{-4} mol/mol-AgX
C-10	0.27 mol/mol-AgX
C-8	0.005 mol/mol-AgX
HBS-1	0.28 g/m^2
Gelatin	1.28 g/m^2

12th Layer (2nd Blue-Sensitive Emulsion Layer):

Silver iodobromide emulsion (silver iodide: 10 mol%; mean grain size: 1.0 μm)	0.45 g of Ag
Sensitizing Dye VIII	2.1x10^{-4} mol/mol-AgX
C-10	0.098 mol/mol-AgX
HBS-1	0.03 g/m^2
Gelatin	0.46 g/m^2

13th Layer (3rd Blue-Sensitive Emulsion Layer):

Silver iodobromide emulsion (silver iodide: 10 mol%; mean grain size: 1.8 μm)	0.77 g of Ag
Sensitizing Dye VIII	2.2x10^{-4} mol/mol-AgX
C-10	0.036 mol/mol-AgX
HBS-1	0.07 g/m^2
Gelatin	0.69 g/m^2

14th Layer (1st Protective Layer):

Silver iodobromide emulsion (silver iodide: 1 mol%; mean grain size: 0.07 μm)	0.5 g of Ag
U-1	0.11 g/m^2
U-2	0.17 g/m^2
HBS-1	0.90 g/m^2

15th Layer (2nd Protective Layer):

Polymethyl methacrylate particles (diameter: ca. 1.5 μm)	0.54 g/m^2
S-1	0.10 g/m^2
S-2	0.10 g/m^2
Gelatin	0.72 g/m^2

Each of the above layers further contained Gelatin Hardener H-1 and a surface active agent.

In the preparation of Sample 101, the coating composition for the 3rd layer was prepared as follows.

In 150 ml of ethyl acetate were dissolved 60 g of Coupler I-13 and 3.4 g of Coupler C-4 under heating, and the solution was mixed with 1000 g of a 10 wt% aqueous solution of gelatin having dissolved therein 5.0 g of sodium dodecylbenzenesulfonate, and the mixture was dispersed in a domestic mixer for 10 minutes.

Samples 102 to 110 were prepared in the same manner as for Sample 101, except that Couplers I-13 and C-4 as used in the 3rd and 4th layers were changed in kind and amount as shown in Table 1 below, and that the gelatin coverage was adjusted so that the film strength of the 3rd layer and that of the 4th layer were equal.

Each of Samples 101 to 110 was imagewise exposed to white light for sensitometry and then subjected to color development processing according to the following procedure at 38°C. The processed sample was determined for density through a red filter. Further, each of the samples was exposed to light through a pattern for MTF measurement and then subjected to the same color development processing to calculate an MTF value at a spatial frequency of 25 c/mm. The results obtained are shown in the Table.

Procedure of Color Development Processing:

Color Development	3'15"
Bleaching	6'30"
Washing	2'10"
Fixation	4'20"
Washing	3'15"
Stabilization	1'05"

The processing solutions used in each processing step had the following formulations.

Color Developer Formulation:

Diethylenetriaminepentaacetic acid	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Sodium sulfite	4.0 g
Potassium carbonate	30.0 g
Potassium bromide	1.4 g
Potassium iodide	1.3 mg
Hydroxylamine sulfate	2.4 g
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g
Water to make	1.0 ℓ
	pH=10.0

Bleaching Solution Formulation:

Ammonium (ethylenediaminetetra-acetato)ferrite	100.0 g
Disodium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Ammonium nitrate	10.0 g
Water to make	1.0 ℓ
	pH=6.0

Fixing Solution Formulation:

Disodium ethylenediaminetetraacetate	1.0 g
Sodium sulfite	4.0 g
Ammonium thiosulfate (70 wt% aqueous solution)	175.0 ml
Sodium bisulfite	4.6 g
Water to make	1.0 ℓ
	pH=6.6

Stabilization Solution:

Formlain (40 wt% formaldehyde)	2.0 ml
Polyoxyethylene-p-monononylphenyl ether (average degree of polymerization: 10)	0.3 g
Water to make	1.0 ℓ

TABLE 1

Sample No.	3rd And 4th Layers Main Coupler 1)	HBS-1/ Total Couplers 2)	Gelatin Coverage (g/m^2)	C-4/ Main Coupler 3)	Relative Sensitivity 4)	Gamma	MTF* (25c/mm)
101	I-13	0	2.70	1	0	0.66	0.56
102	"	0.04	2.85	0.95	-0.01	0.65	0.55
103	"	0.20	3.40	0.85	0.00	0.66	0.53
104	"	0.40	4.30	0.60	+0.01	0.67	0.49
105	"	1.0	5.80	0.40	-0.01	0.65	0.47
106	C-2	0	2.70	1	-0.16	0.39	- 5)
107	"	0.04	2.85	0.95	-0.16	0.40	- 5)
108	"	0.20	3.40	0.85	-0.15	0.42	0.51
109	"	0.40	4.30	0.60	-0.08	0.58	0.49
110	"	1.00	5.80	0.40	-0.01	0.67	0.47

* MTF: Modulation transfer function

Note:

1) Colorless coupler of the 3rd and 4th layers other than colored couplers and DIR compounds.

2) Weight ratio of HBS-1 (high-boiling point organic solvent) to the main cyan coupler of the present invention.

3) Relative ratio of DIR coupler to the main coupler of the present invention, taking that of Sample l0l as l (standard).

4) Relative logarithm of a reciprocal of an exposure providing a cyan dye density of fog + 0.5, taking that of Sample 101 as O (standard).

5) Fine crystals were observed in the sample, and the MTF measurement was impossible.

It can be seen from Table 1 that the comparative samples, in which a cyan coupler out of the scope of the present invention is dispersed with the aid of a high-boiling organic solvent, undergo precipitation of the coupler as observed in Samples 106 and 107 or reduction of color developability as observed in Sample 108, while all the samples according to the present invention (Samples 101 to 103) exhibit satisfactory color developability. It is also apparent that Samples 101 to 103 show obviously increased MTF values indicative of improved sharpness as compared with Sample 104 or 105 in which the coupler within the scope of the present invention is combined with a large amount of the high-boiling point organic solvent.

EXAMPLE 2

Sample 201 was prepared in the same manner as for Sample 101 of Example 1, except for replacing Coupler C-4 in the 3rd and 4th layers with one-half the molar quantity of C-14, replacing Coupler C-5 in the 5th layer with two-third the molar quantity of Coupler I-14, and further replacing Coupler C-9 in the 9th layer with one-half the molar quantity of Coupler C-15.

Samples 202 to 206 were prepared in the same manner as for Sample 201, except that the main coupler in the 3rd and 4th layers, Coupler I-13, was replaced with the equimolar amount of each of Couplers I-11, I-3, I-53, C-11, and C-13, respectively.

Sample 207 was prepared in the same manner as for Sample 201, except for replacing the main coupler in the 7th and 8th layers, Coupler C-6, with double the molar amount of Coupler C-16 and using an additional amount of gelatin to make the film strength of both layers equal.

Sample 208 was prepared in the same manner as for Sample 201, except that the main coupler of the 7th and 8th layers, Coupler C-6, was replaced with double the molar amount of Coupler C-9 and the amount of the organic solvent was doubled to make the color developability and preservability substantially equal to those of Sample 201.

Each of Samples 201 to 208 was exposed to light and development-processed in the same manner as described in Example 1. The processing of Example 1 is herein designated as Processing A. The sensitivity, gamma, and MTF values of the processed samples were determined. In addition, the cyan density of the processed samples on the point having been exposed at an exposure of 1 $\times$ 20^{-3} CMS was also measured. The results obtained are shown in Table 2 below.

Further, the same procedure was repeated, except for replacing the bleaching solution as used in Processing A with a bleaching solution prepared as follows. This processing is designated as Processing B. The bleaching solution used in Processing B was designed to be a model of a fatigued processing solution after use for processing a large quantity of light-sensitive materials.

The samples having been processed according to Processing B were determined for cyan density in the same manner as described above. The results obtained are also shown in the Table.

Preparation of Bleaching Solution for Processing B:

(D-1)	Ammonium bromide	160.0 g
	Aqueous ammonia (28 wt%)	7.1 ml
	Sodium (ethylenediaminetetraacetato)iron	117 g
	Glacial acetic acid	14 ml
	Water to make	900 ml
(D-2)	Sodium (ethylenediaminetetraacetato)iron	130 g
	Water to make	1000 ml

Steel wool was poured into (D-2), and the preparation was sealed and left to stand to allow Fe(III)-EDTA to be converted to Fe (II)-EDTA. A 100 ml portion of the resulting solution was added to (D-1).

TABLE 2

Sample No.	Main Coupler	Relative Sensitivity*	Gamma*	MTF* (25c/mm)	Cyan Density at Point Exposed at 1 x 10^{-3} CMS Process-ing A	Process-ing B	Processing (B)/ Processing (A)
201	I-13	0	0.68	0.57	1.20	1.18	0.98
202	I-11	+0.01	0.70	0.56	1.23	1.20	0.98
203	I-3	0	0.67	0.57	1.20	1.19	0.99
204	I-53	+0.01	0.67	0.57	1.19	1.18	0.99
205	C-11			unmeasurable**			
206	C-13	-0.02	0.61	0.56	1.14	0.76	0.67
207	I-13	+0.01	0.70	0.54	1.21	1.19	0.98
208	I-13	+0.01	0.69	0.52	1.21	1.20	0.99

Note: *: Measured in the same manner as in Example 1.

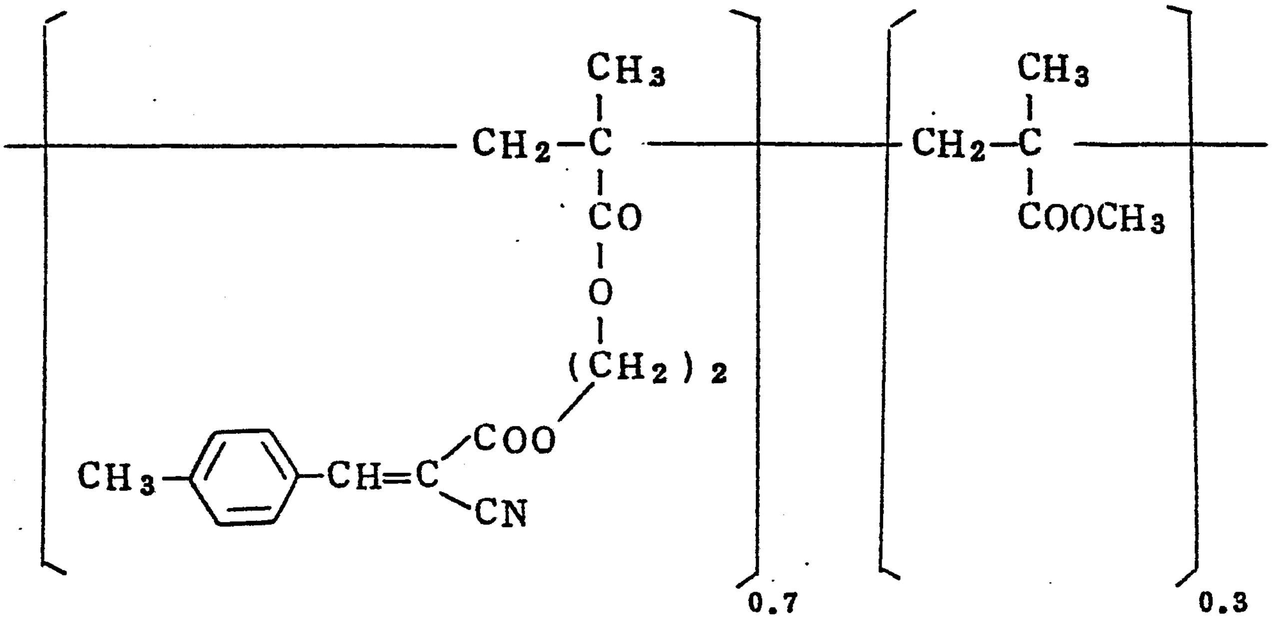
**: The emulsion had poor dispersion stability and a large amount of fine crystals was precipitated in the sample so that sensitometry and MTF measurement were impossible.

From Table 2, the following observations can be made. Sample 205 using the comparative coupler showed an extremely low color density so that the relative sensitivity, gamma, and MTF value were unmeasurable. Sample 206 shows considerable reduction in cyan color density when processed with a fatigued bleaching solution.

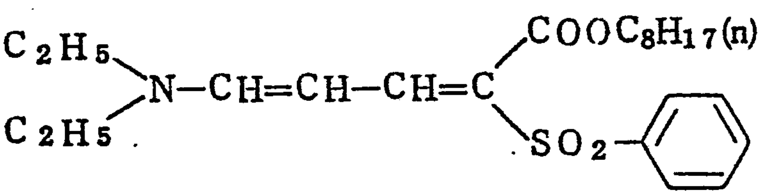
On the other hand, Samples 201 to 204 according to the present invention sufficiently satisfy these performance requirements, clearly demonstrating the effectiveness of the present invention. Further, it can be seen that Samples 207 or 208, in which a 4-equivalent polymeric magenta coupler (C-16) or a 4-equivalent magenta coupler (C-9) was used, respectively, in the 7th and 8th layers, shows a slightly reduced MTF value. In other words, the effects of the cyan couplers of the invention to improve sharpness can be ensured by using 2-equivalent magenta couplers in combination rather than 4-equivalent magenta couplers.

The compounds used in the sample preparation of Examples 1 and 2 are as follows.

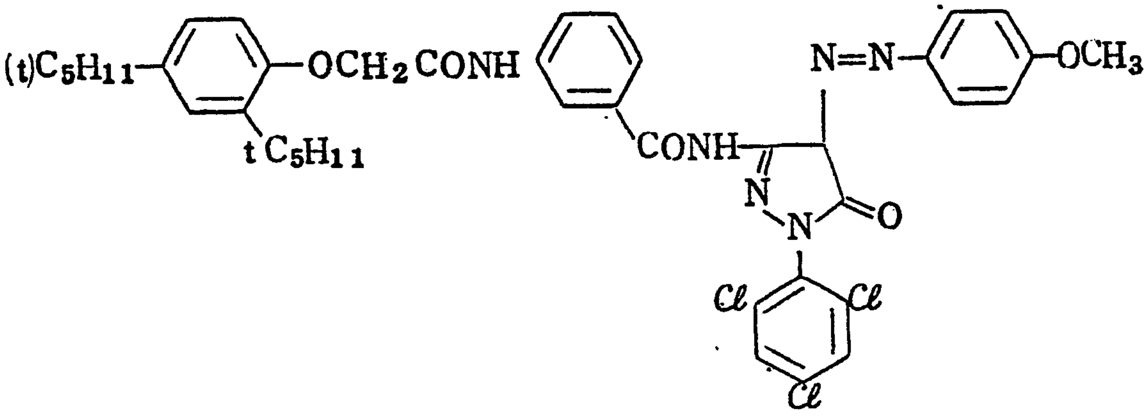
U – 1



U – 2

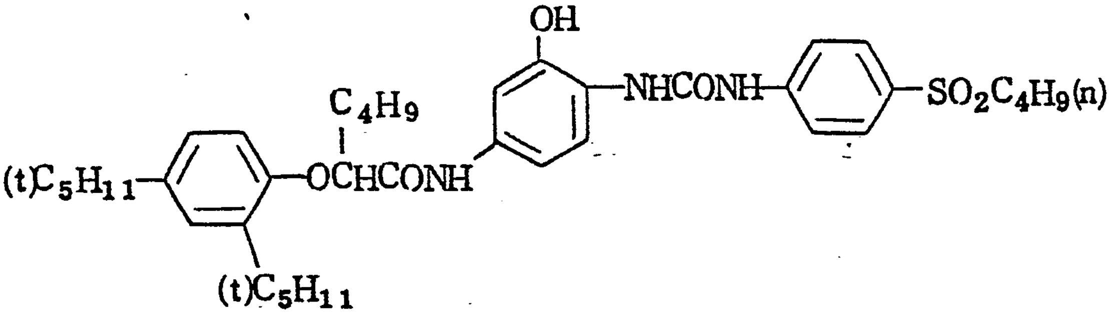


C - 1

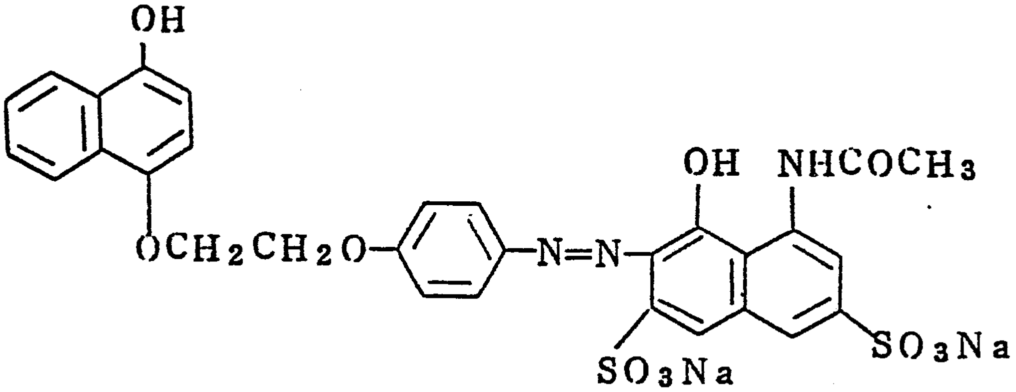


C - 2

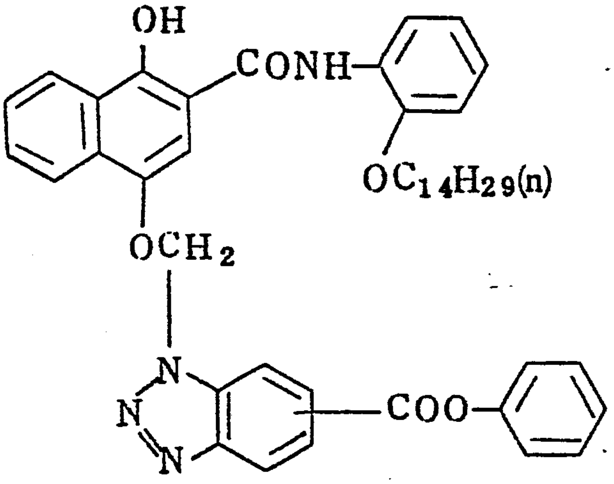
(Coupler as described in Japanese Patent Application (OPI) No. 204545/82)



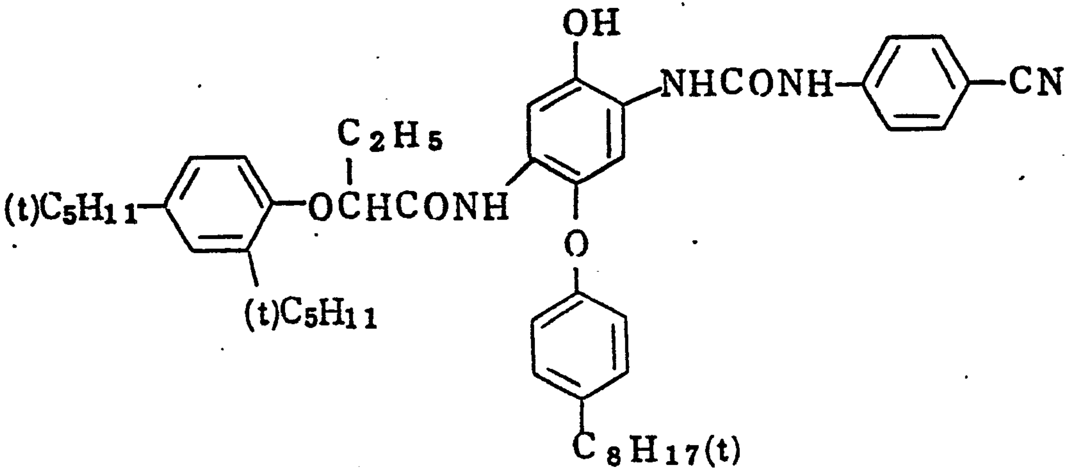
C – 3


OH
OCH₂CH₂O
N=N
OH
NHCOCH₃
SO₃Na
SO₃Na

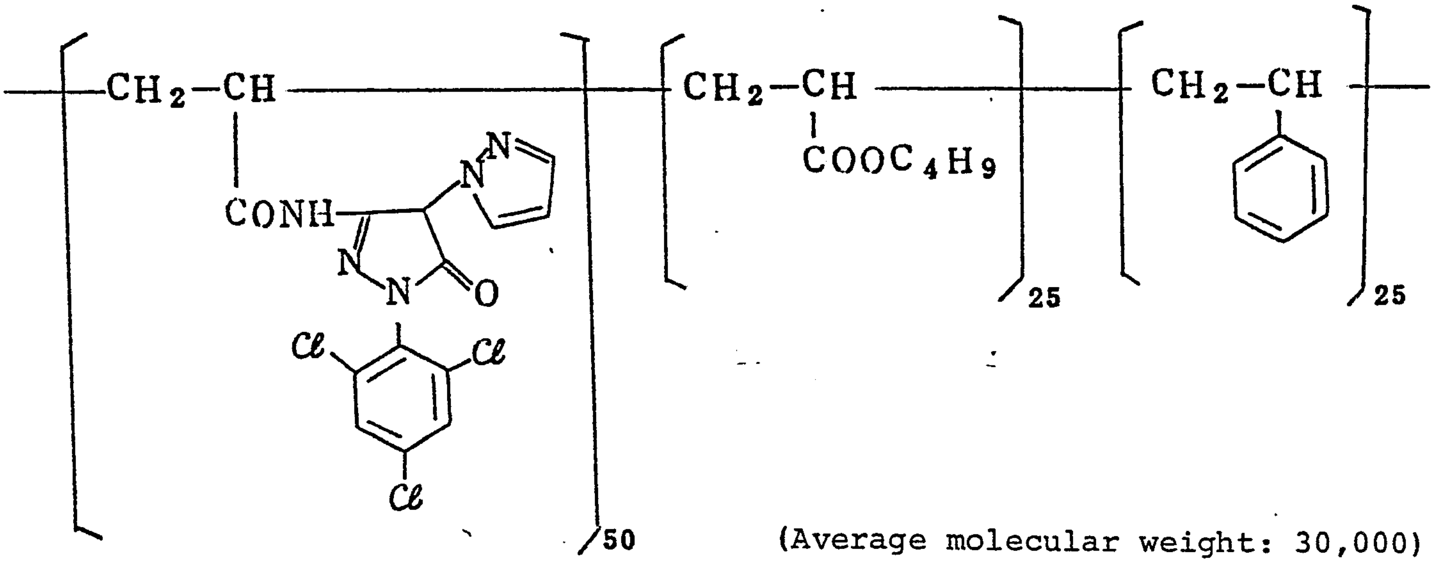
C – 4


OH
CONH
OC₁₄H₂₉(n)
OCH₂
N
N
N
COO

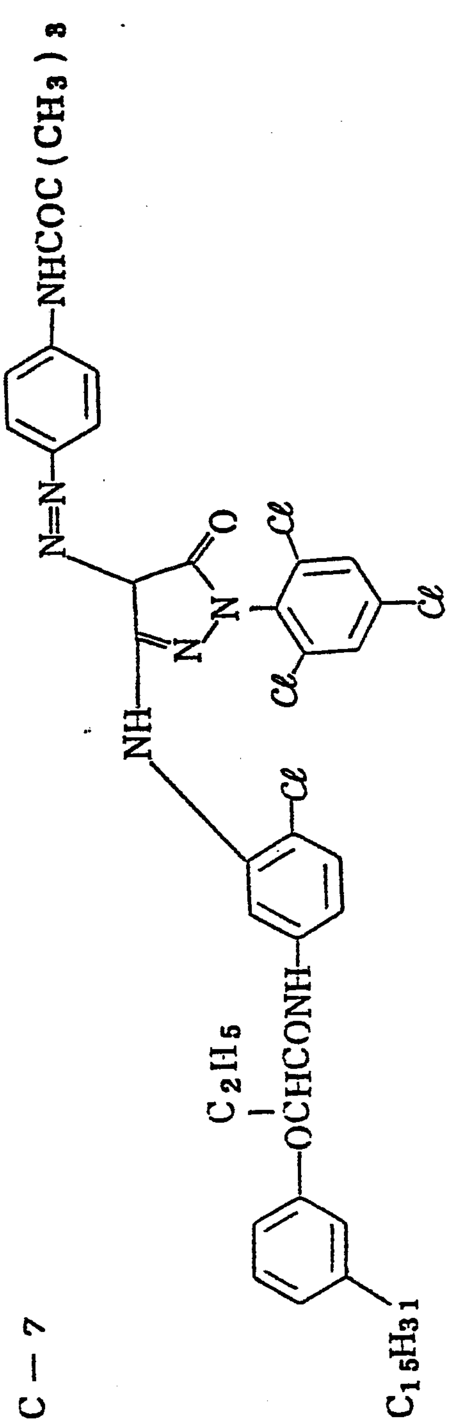
C - 5



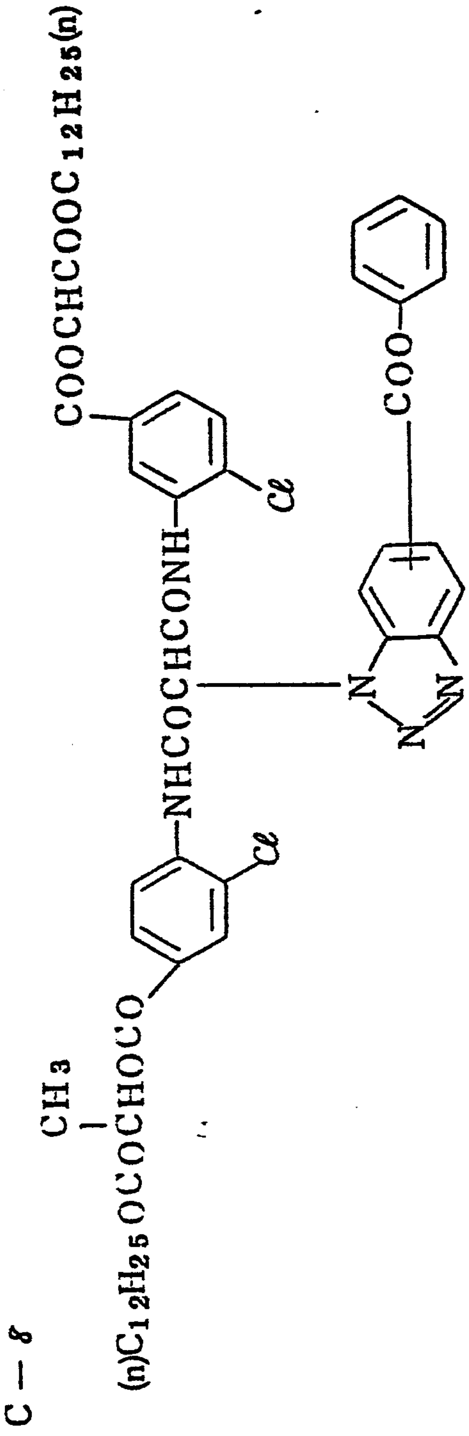
C - 6 (P - 1 3)



(Average molecular weight: 30,000)

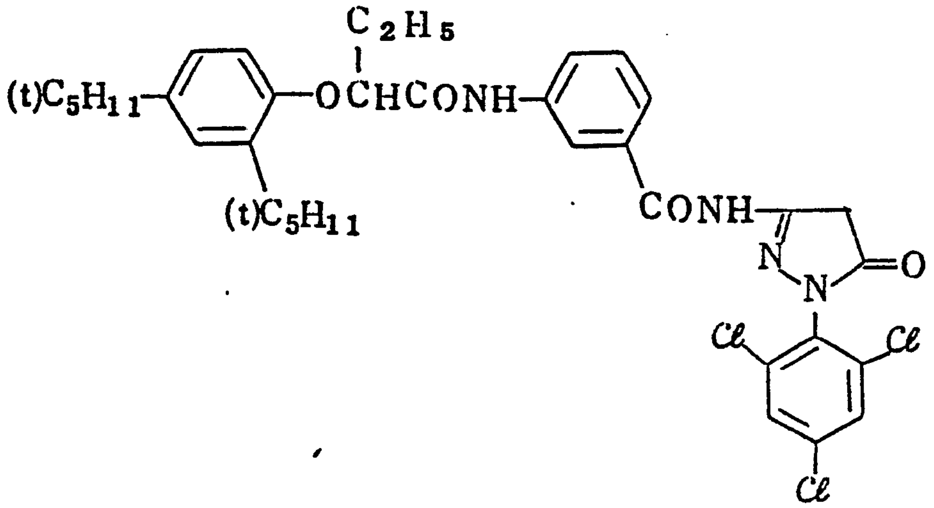


C — 7

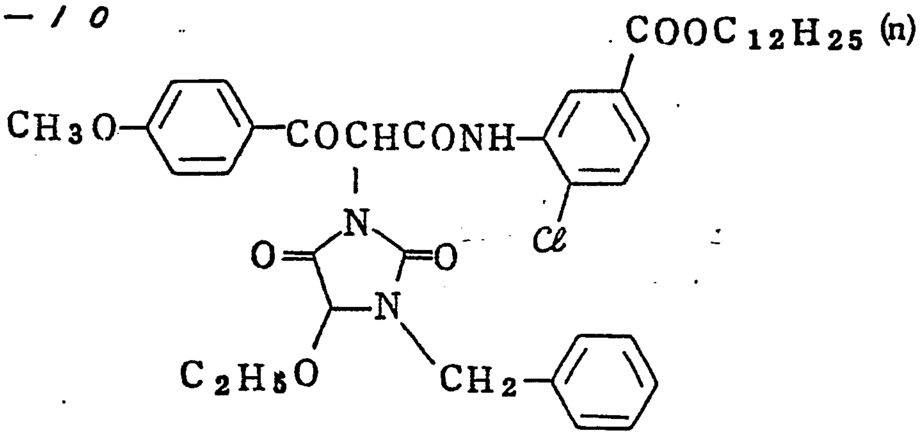


C — 8

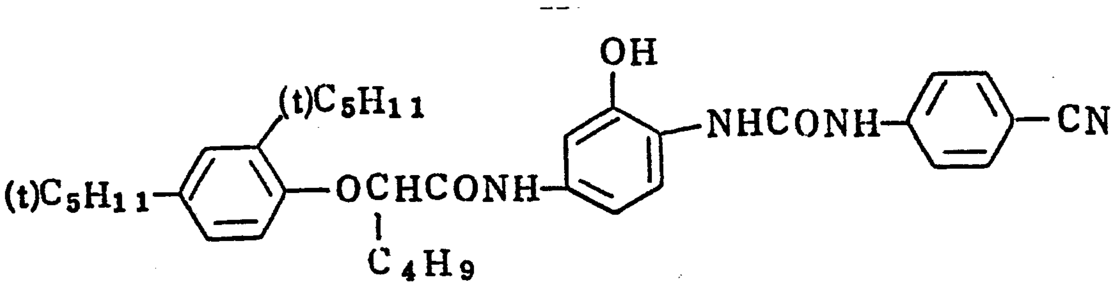
C − 9



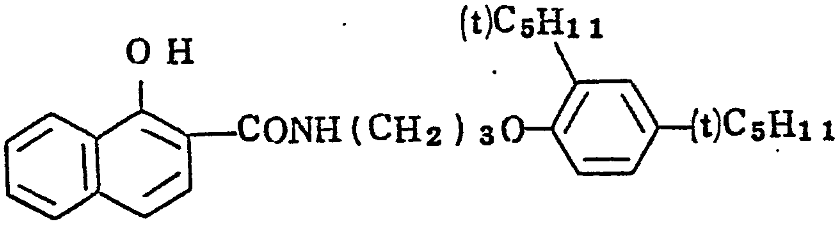
C − 10



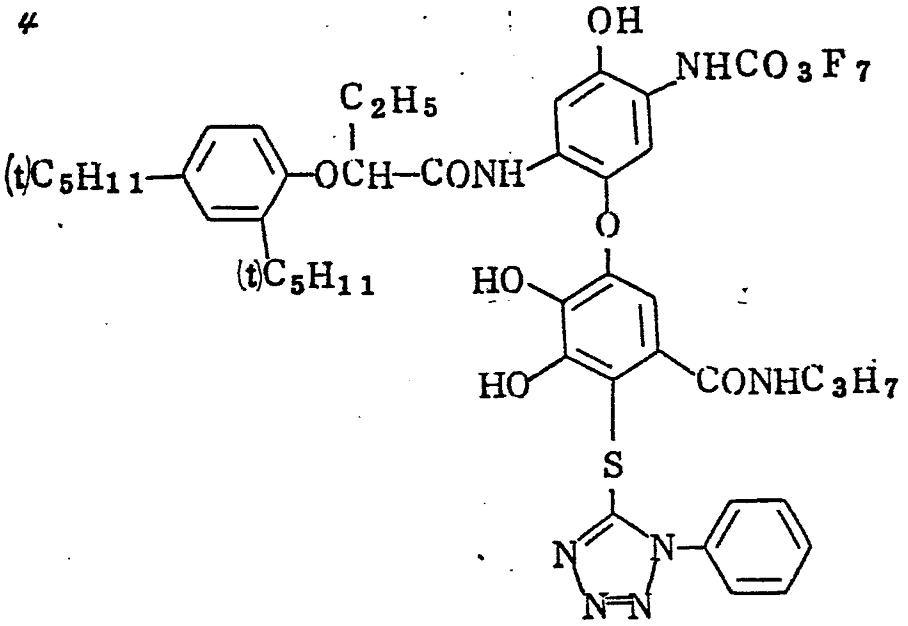
C-11 (Coupler 7 as described in U.S. Patent 4,333,999)



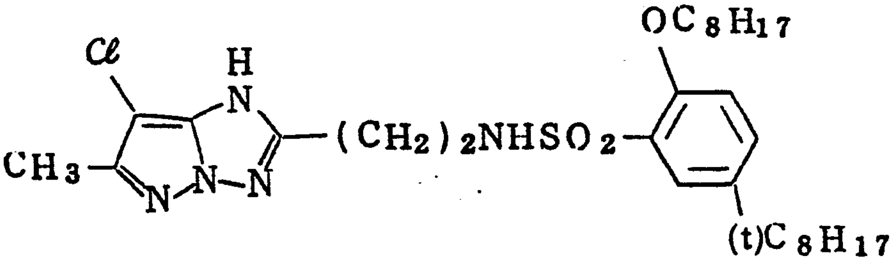
C-13



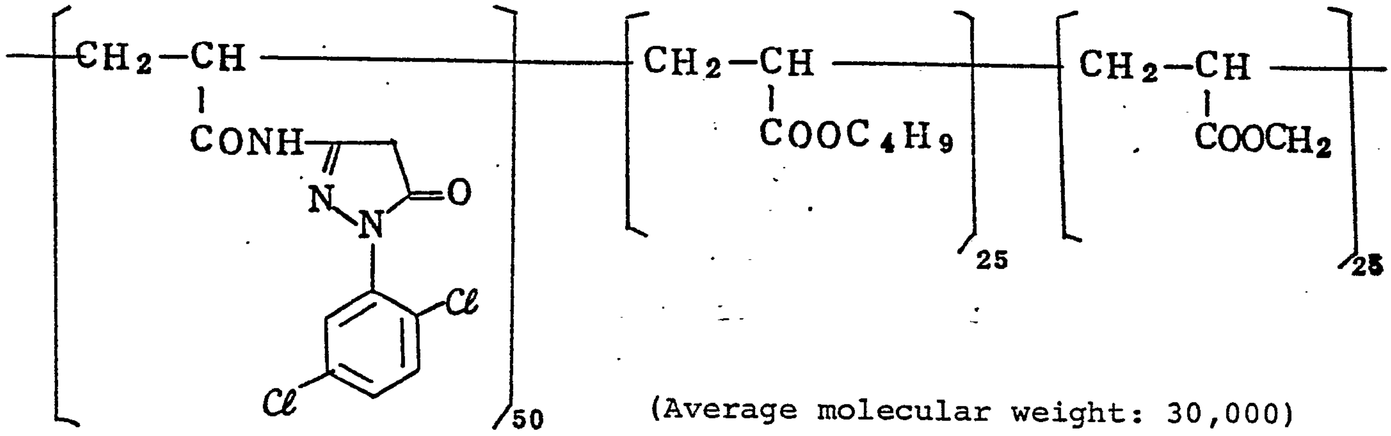
C-14



C－15

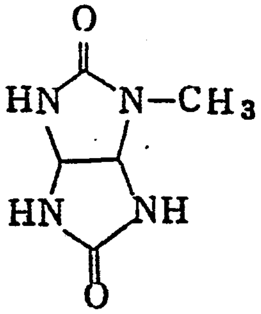


C－16 (P－14)

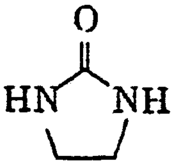


(Average molecular weight: 30,000)

S-1

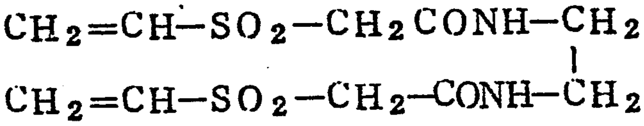


S-2



HBS-1	Tricresyl phosphate
HBS-2	Dibutyl phthalate

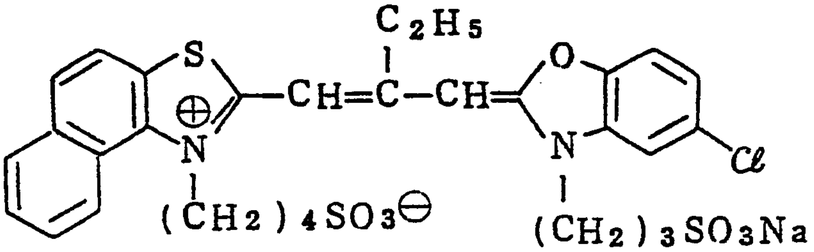
H-1



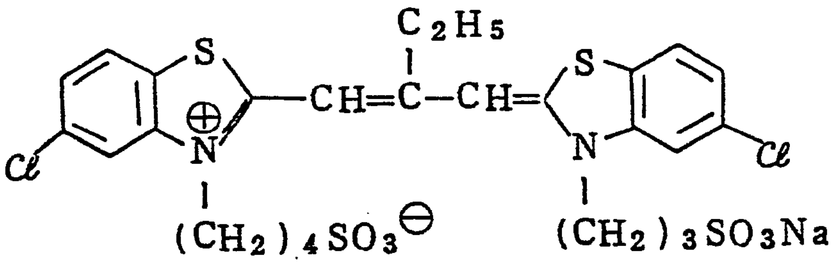
$$\begin{array}{l} CH_2{=}CH{-}SO_2{-}CH_2CONH{-}CH_2 \\ \hphantom{CH_2{=}CH{-}SO_2{-}CH_2CONH{-}C}| \\ CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \end{array}$$

Sensitizing Dye

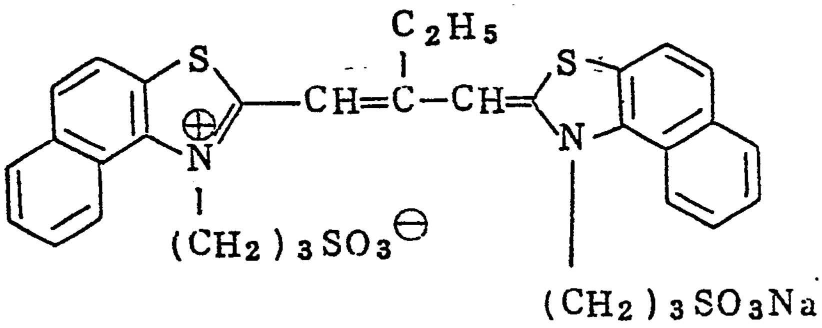
I



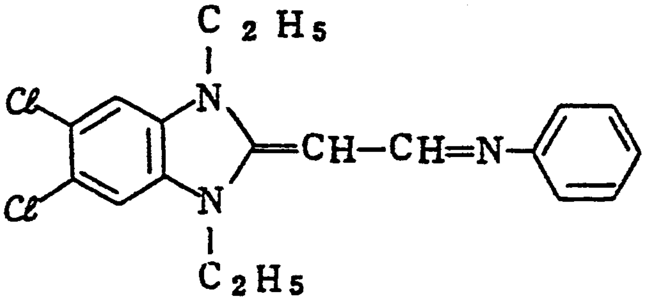
II



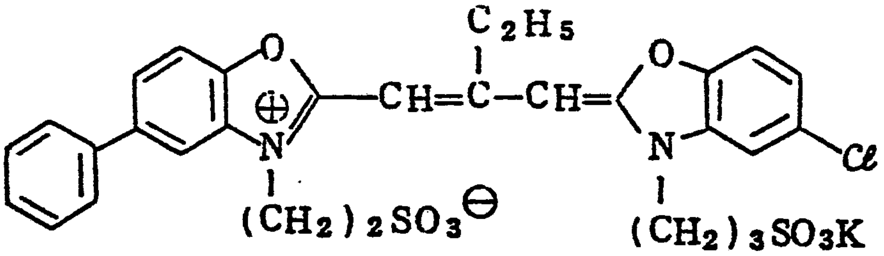
III



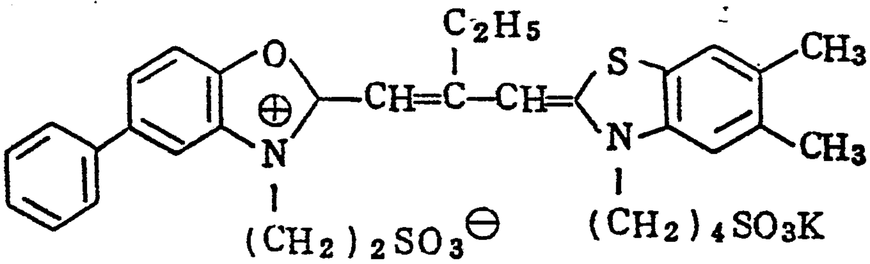
IV



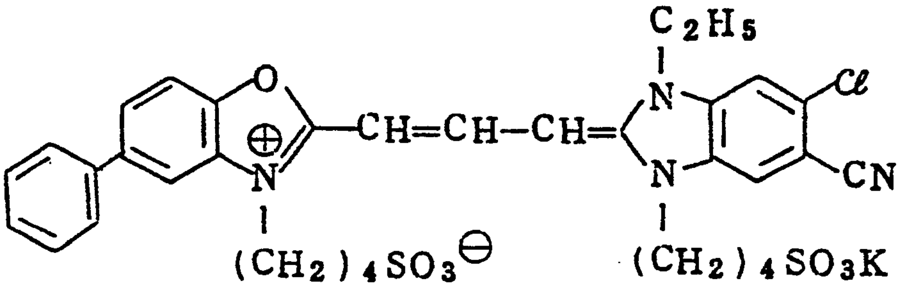
V



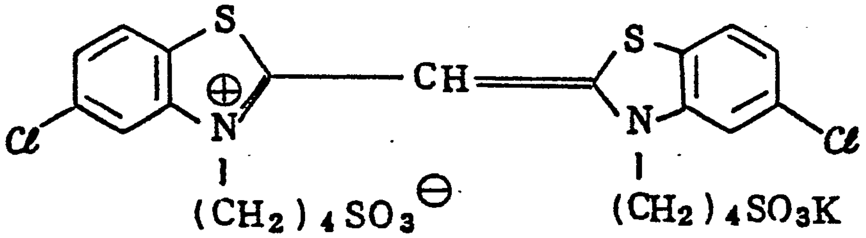
VI .



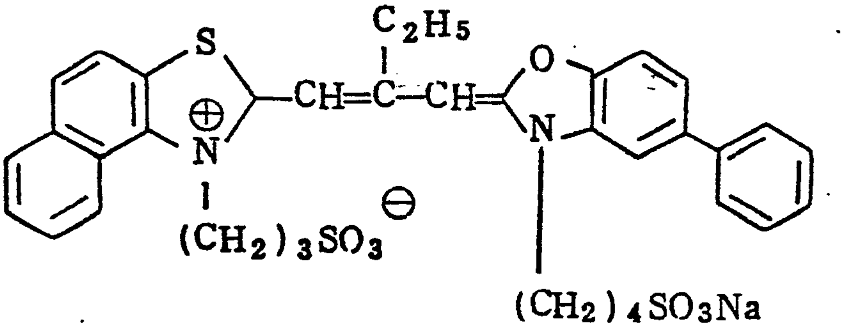
VII


C2H5
N
Cl
O
⊕
N
CH=CH–CH=
N
CN
(CH2)4SO3⊖
(CH2)4SO3K

VIII


S
⊕
N
CH=
S
N
Cl
Cl
(CH2)4SO3⊖
(CH2)4SO3K

IX

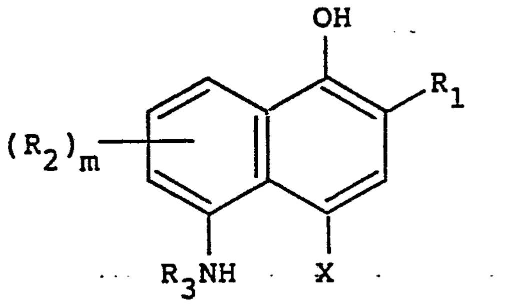

C2H5
S
⊕
N
CH=C–CH=
O
N
(CH2)3SO3⊖
(CH2)4SO3Na

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

Claims

1. A silver halide color photographic material comprising a support having provided thereon at least one silver halide emulsion layer containing a cyan coupler, at least one silver halide emulsion layer containing a magenta coupler, and at least one silver halide emulsion layer containing a yellow coupler, wherein said cyan coupler-containing emulsion layer contains

(I) at least one cyan coupler represented by formula (I)



(I)

wherein R_1 represents $-CONR_5R_6$, $-NHCOR_5$, $-NHCOOR_7$, $-NHSO_2R_7$, $-NHCONR_5R_6$ or $-NHSO_2NR_5R_6$, wherein R_5 and R_6 each represents a hydrogen atom, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group, or a substituted or unsubstituted heterocyclic group, or R_5 and R_6 together form a nitrogen-containing heterocyclic ring, and R_7 represents a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group, or a substituted or unsubstituted heterocyclic group; R_2 represents a group capable of substituting for a hydrogen atom of a naphthalene ring, or a plurality of R_2 groups together form a ring; m represents 0 or an integer of from I to 3; R_3 represents a monovalent organic group; and X represents a hydrogen atom or a group releasable upon coupling with an oxidation product of an aromatic primary amine developing agent, or R_3 together with R_2 or X forms a ring; or R_1, R_2, R_3, or X forms a polymer including a dimer via a divalent group; and

(2) a high boiling point organic solvent in an amount of not more than 30% by weight based on the total amount of said at least one cyan coupler represented by formula (I).

2. A silver halide color photographic material as in claim I, wherein R_1 represents $CONR_5R_6$.

3. A silver halide color photographic material as in claim I, wherein R_2 represents a halogen atom, a substituted or unsubstituted aliphatic group, a carbonamido group, or a sulfonamido group.

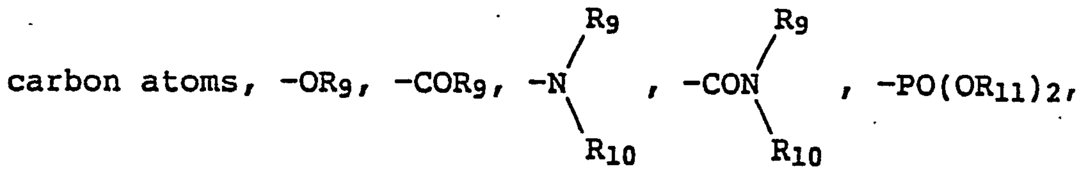
4. A silver halide color photographic material as in claim I, wherein m is 0.

5. A silver halide color photographic material as in claim I, wherein R_3 is represented by formula (II)

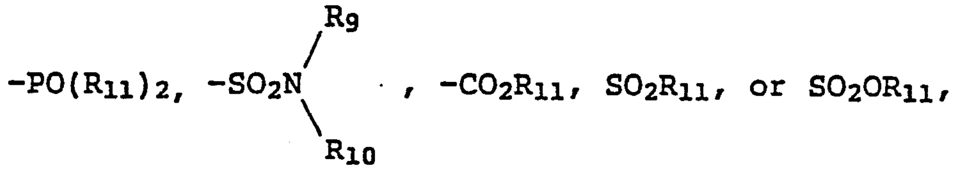
$R_8(Y)_n-$ (II)

wherein Y represents $>NH$, $>CO$, or $>SO_2$

n represents 0 or I; and R_8 represents a hydrogen atom, a substituted or unsubstituted aliphatic group having from I to 30 carbon atoms, a substituted or unsubstituted aromatic group having from 6 to 30 carbon atoms, a substituted or unsubstituted heterocyclic group having from 2 to 30



carbon atoms, $-OR_9$, $-COR_9$, $-N(R_9)(R_{10})$, $-CON(R_9)(R_{10})$, $-PO(OR_{11})_2$,



$-PO(R_{11})_2$, $-SO_2N(R_9)(R_{10})$, $-CO_2R_{11}$, SO_2R_{11}, or SO_2OR_{11},

wherein R_9, R_{10}, and R_{11} each represents a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group, or a substituted or unsubstituted heterocyclic group, or R_9 and R_{10} together form a nitrogen-containing heterocyclic group.

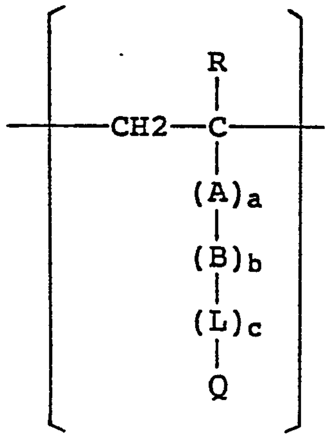
6. A silver halide color photographic material as in claim 5, wherein n is 0, and R_8 represents $-COR_9$, $-COOR_{11}$, $-SO_2R_{11}$, $-CONR_9R_{10}$, or $-SO_2NR_9R_{10}$, wherein R_9, R_{10}, and R_{11} are the same as defined in claim 5.

7. A silver halide color photographic material as in claim 6, wherein R_8 represents $-COOR_{11}$, $-COR_9$, or $-SO_2R_{11}$, wherein R_9 and R_{11} are the same as defined in claim 5.

8. A silver halide color photographic material as in claim 7, wherein R_8 represents $-COOR_{11}$, wherein R_{11} is the same as defined in claim 5.

9. A silver halide color photographic material as in claim l, wherein X represents a hydrogen atom, a chlorine atom, an aliphatic oxy group, an aromatic oxy group, or a carbamoyloxy group.

l0. A silver halide color photographic material as in claim l, wherein said polymer comprises a repeating unit represented by formula (III)



(III)

$$\left[-CH_2-C(R)\left((A)_a-(B)_b-(L)_c-Q\right)- \right]$$

wherein R represents a hydrogen atom, an alkyl group having from l to 4 carbon atoms, or a chlorine atom; A represents -CONH-, -COO-, or a substituted or unsubsti tuted phenylene group; B represents a substituted or unsubstituted alkylene, phenylene, or aralkylene group; L represents -CONR'-, -NR'CONR'-, -NR'COO-, -NR'CO-, -OCONR'-, -NR'-, -COO-, -OCO-, -CO-, -O-, SO_2-, $-NR'SO_2$-, or $-SO_2NR'$-, wherein R' represents a hydrogen atom or a substituted or unsubstituted alkyl or aryl group; a, b, and c each represents 0 or l; and Q represents a cyan coupler residual group derived from formula (I) by removing any one of hydrogen atoms other than the hydrogen atom of the l-positioned hydroxyl group.

ll. A silver halide color photographic material as in claim l, wherein said high boiling point organic solvent has a boiling point of l75°C or higher.

l2. A silver halide color photographic material as in claim l, wherein said high boiling point organic solvent is selected form phosphoric esters and phthalic esters.

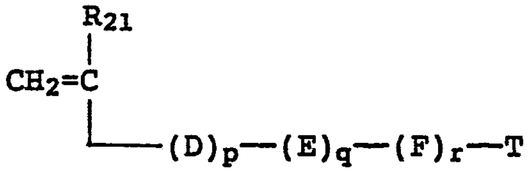
l3. A silver halide color photographic material as in claim l, wherein said high boiling point organic solvent is present in an amount of not more than l5% by weight based on the total amount of said cyan coupler represented by formula (I).

14. A silver halide color photographic material as in claim 13, wherein said high boiling point organic solvent is present in an amount of not more than 5% by weight based on the total amount of said cyan coupler represented by formula (I).

15. A silver halide color photographic material as in claim 14, wherein said high boiling point organic solvent is present in an amount of not more than 1% by weight based on the total amount of said cyan coupler represented by formula (I).

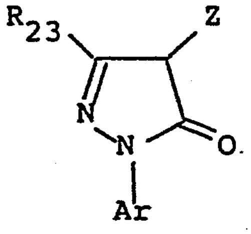
16. A silver halide color photographic material as in claim 1, wherein said magenta coupler is a 2-equivalent polymeric magenta coupler.

17. A silver halide color photographic material as in claim 16, wherein said 2-equivalent polymeric magenta coupler comprises a repeating unit derived from a compound represented by formula (IV)



$$CH_2{=}C(R_{21})\text{—}(D)_p\text{—}(E)_q\text{—}(F)_r\text{—}T \qquad \text{(IV)}$$

wherein R_{21} represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms, or a chlorine atom; D represents -COO-, $-CONR_{22}-$, or a substituted or unsubstituted phenyl group; E represents a substituted or unsubstituted alkylene, phenylene, or aralkylene group having from 1 to 10 carbon atoms; F represents $-CONR_{22}-$, $-NR_{22}CONR_{22}-$, $-NR_{22}COO-$, $-NR_{22}CO-$, $-OCONR_{22}-$, $-NR_{22}-$, -COO-, -OCO-, -CO-, -O-, -S-, $-SO_2-$, $-NR_{22}SO_2-$, or $-SO_2NR_{22}-$, wherein R_{22} represents a hydrogen atom or a substituted or unsubstituted aliphatic or aryl group; p, q, and r each represents 0 or 1; and T represents a coupler residual group derived from a magenta coupler represented by formula (V)



(V)

wherein Ar represents an alkyl group, a heterocyclic group, or an aryl group; R_{23} represents a substituted or unsubstituted anilino group, a substituted or unsubstituted acylamino group, a substituted or unsubstituted ureido group, or a substituted or unsubstituted sulfonamido group; and Z represents a hydrogen atom, a halogen atom, a coupling releasable group bonded via an oxygen atom, a coupling releasable group bonded via a nitrogen atom, or a coupling releasable group bonded via a sulfur atom.