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

(57) Silver halide color photographic material contains lipophilic polymeric couplers. The said lipophilic polymeric couplers are obtained by polymerization reaction using a chain transfer agent having at least 8 carbon atoms and a chain transfer constant with respect to the monomeric coupler is at least 0.1 but not more than 20.

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SILVER HALIDE COLOR PHOTOGRAPHIC MATERIALS

FIELD OF THE INVENTION

This invention concerns silver halide color photographic materials which contain novel colored image forming couplers which can couple with the oxidized form of a primary aromatic amine developing agent.

BACKGROUND OF THE INVENTION

It is known that primary aromatic amine developing agents which have been oxidized in the post exposure development process react with a coupler in silver halide color photographic materials to form a colored image with indophenol, indoaniline, indamine, azomethine, phenoxazine, phenazine or similar dyes. The subtractive color method is used for normal color reproduction in this way, and silver halide emulsions which have been sensitized selectively to blue, green and red light and which contain complementary yellow, magenta and cyan colored image forming agents are used in these materials.

However, in the case of a multi-layer color photosensitive material, the respective couplers have to be fixed in separate layers in order to minimize color mixing and to provide good color reproduction. A number of known methods are available for rendering couplers fast to diffusion.

In one such method, long chain aliphatic groups are introduced into a low molecular weight coupler in order to impede diffusion. Couplers obtained using this method do not mix with aqueous gelatin solutions and so they must be rendered soluble in alkali for addition to a gelatin solution, or alternatively they must be dissolved in an organic solvent of high boiling point for emulsification and dispersion in an aqueous gelatin solution.

Color couplers of this type may precipitate crystals in the emulsion or, in cases where an organic solvent of high boiling point is used, the emulsion layer may become soft and so large amounts of gelatin are required, and this is contrary to the requirements of thinner emulsion layers. In another method for introducing couplers into separate layers use is made of polymer latexes obtained by the polymerization of monomeric couplers.

The method in which these polymeric couplers are added in the form of a latex to a hydrophilic colloid composition has many advantages over the other method.

Thus, first of all there is no deterioration of the strength of the film which is formed because the hydrophobic material is present in the form of a latex. Furthermore, it is possible to include a high concentration of coupler units in the latex and so a high concentration of coupler can be included in the emulsion without difficulty, and since the increase in viscosity is small, the film can be reduced in thickness and sharpness can be improved.

Moreover, since the couplers are immobile there is no color mixing and little precipitation of the coupler within the emulsion layer.

Polymeric couplers in the form of a latex of this type for addition to gelatin/silver halide emulsions include four equivalent magenta polymeric couplers, the methods for their manufacture have been disclosed, for example, in U.S. Patent 4,080,211, British Patent 1,247,668 and U.S. Patent 3,451,820, the copolymer latexes with competitive couplers which have been disclosed in West German Patent 2,725,591 and U.S. Patent 3,926,436, and the cyan polymeric latexes which have been disclosed in U.S. Patent 3,767,412 and Research Disclosure 21728 (1982).

However, although these polymeric couplers have the excellent features such as those aforementioned, they also are in need of improvement as regards the following aspects:

1. Polymeric couplers of 'comparatively high molecular weight (of number average molecular weight above about 10,000) have adequate immobility but, because of their poor coupling reactivity, the sensitivity and gradation of the dyes which are formed and the dye density are low.

2. If the coupler unit content (the content of repeating units which have coupler residual groups) in the polymeric coupler is increased the color forming ability per unit weight (of coupler unit) is markedly reduced.

3. On the other hand, the dye density is increased with polymeric couplers which have been reduced in molecular weight, but color mixing and a loss of speed occur because these polymeric couplers are inadequate in respect of immobility.

If it were possible to retain a high color forming ability with a polymeric coupler which has a high coupler unit content it would be possible to reduce the layer thickness of the sensitive material, since a small amount of coupler at high concentration could be included in the emulsion, and so improvement of the color forming ability in polymeric coupler which have a high coupler unit content is clearly of importance and desired.

Furthermore, the provision of both immobility and coupling reactivity in a polymeric coupler is also of importance.

SUMMARY OF THE INVENTION

Hence, the main task of the invention is to provide high speed silver halide color photographic materials containing, novel polymeric couplers which have a high coupler unit content and which exhibit a high color forming ability.

A further task of the invention is to provide silver halide color photographic materials in which there is no color mixing because of the immobility of the couplers.

Another task of the invention is to provide a method of forming colored images having excellent quality, in particular light color density.

The task of the invention are achieved by means of a silver halide color photographic material containing in at least one silver halide emulsion layer and/or in at least one layer adjacent thereto at least one lipophilic polymeric coupler, characterized in that said lipophilic polymeric coupler is obtained by a polymerisation reaction using a chain transfer agent having at least 8 carbon atoms and a chain transfer constant with respect to the respective monomeric coupler in the range of from 0.1 to 20.

The novel lipophilic polymeric couplers synthesized by means of a polymerization reaction using chain transfer agents having at least 8 carbon atoms and chain transfer constants for the monomeric couplers of at least 0.1 but not more than 20 are mixtures of polymers of various structures, but in the main they can be represented by the general formula [P] which is indicated below.

General Formula [P]

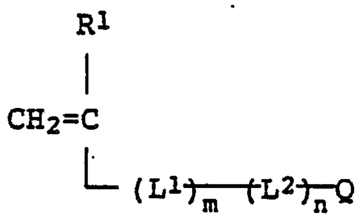
$$E\text{-}(A)_x\text{—}(B)_y\text{—}X$$

E represents a univalent group originating from the radical part which is formed by chain transfer to a chain transfer agent which has at least 8 carbon atoms and of which the chain transfer constant with respect to the monomeric coupler is at least 0.1 but not more than 20. A represents a repeating unit which is derived from an ethylenically unsaturated monomer which has a coupler residual group which can couple with the oxidized form of a primary aromatic amine developing agent and form a dye. B represents a repeating unit derived from a copolymerizable ethylenically unsaturated monomer. X represents a univalent group. Moreover, x and y are the contents of each type of repeating units in the polymeric coupler, and the weight ratio of x and y (x:y) is from 10:90 to 100:0.

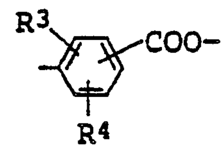
Compounds of this invention which can be represented by the general formula [P] are described in more detail below.

Thus A is a repeating unit which has a coupler residual group which can couple with the oxidized form of a primary aromatic amine developing agent and form a dye, as mentioned above, and it is derived from a monomer which can be represented by the general formula [I] indicated below.

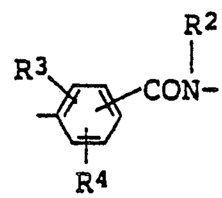
General Formula [I]



In this formula, R^1 represents a hydrogen atom, an alkyl group which has from 1 to 4 carbon atoms or a chlorine atom, and L^1 represents a $-CO\overset{R^2}{\overset{|}{N}}-$ group (where R^2 represents an alkyl group which has from 1 to 4 carbon atoms or a substituted alkyl group which has from 1 to 6 carbon atoms), a -COO- group, an -NHCO- group, an -OCO- group, an



group (where R^3 and R^4 each independently represent a hydrogen atom, hydroxyl group, halogen atom or a substituted or unsubstituted alkyl, alkoxy, acyloxy or aryloxy group), an



group (where R^2, R^3 and R^4 have the same meaning as above), L^2 represents a linking group which links Q with L^1, m represents 0 or 1, n represents 0 or 1, and Q represents a coupler residual group which can couple with an oxidized primary aromatic amine developing agent to form a dye.

The linking group represented by L^2 is typically represented by the formula:

$$\{ X' (J'-X^2)_p (J^2-X^3)_q (J^3)_r \}_s$$

J^1, J^2 and J^3 may be the same of different, each representing, for example, a -CO- group, $-SO_2$ group, $-CO\overset{R^5}{\overset{|}{N}}$ group (where R^5 represents a hydrogen group, alkyl group (which has from 1 to 6 carbon atoms), substituted alkyl group (which has from 1 to 6 carbon atoms)), $-SO_2\overset{R^5}{\overset{|}{N}}$ group (where R^5 has the same meaning as described above), $-\overset{R^5}{\overset{|}{N}}-R^6-$ group (where R^5 has the same meaning as described above and R^6 is an alkylene group which has from 1 to about 4 carbon atoms, an $-\overset{R^5}{\overset{|}{N}}-R^6-\overset{R^7}{\overset{|}{N}}-$ group (where R^5 and R^6 have the same meaning as described above and R^7 represents a hydrogen atom, an alkyl group (which has from 1 to 6 carbon atoms) or a substituted alkyl group (which has from 1 to 6 carbon atoms)), -O- group, -S- group, $-\overset{R^5}{\overset{|}{N}}-CO-\overset{R^7}{\overset{|}{N}}-$ group (where R^5 and R^7 have the same meaning as described above, $-\overset{R^5}{\overset{|}{N}}-SO_2-\overset{R^7}{\overset{|}{N}}-$ group (where R^5 and R^7 have the same meaning as described above), -COO- group, -OCO- group,

- $\overset{R^5}{\overset{|}{N}}CO_2$- group (where R^5 has the same meaning as described above),
- $\overset{R^5}{\overset{|}{N}}CO$- group (where R^5 has the same significance as described above).

· X^1, X^2 and X^3 may be the same Or different, each representing an alkylene group, substituted alkylene group, arylene group, substituted arylene group, aralkylene group or substituted aralkylene group.

Moreover p, q, r and s each represent 0 or 1.

In the above mentioned general formula [I], X^1, X^2 and X^3 may be the same or different, each representing a substituted or unsubstituted alkylene group which has from 1 to 10 carbon atoms, aralkylene having 7 to 20 carbon atoms, or a phenylene group having 6 to 20 carbon atoms, and the alkylene groups may be linear chain or branched groups. Examples of alkylene groups include methylene, methylmethylene, dimethylmethylene, dimethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene and decylmethylene groups, the benzylidene group is an example of an aralkylene group, and examples of phenylene groups include p-phenylene, m-phenylene and methylphenylene groups.

Furthermore, substituent groups for the alkylene groups, aralkylene groups and arylene groups represented by X^1, X^2 and X^3 include halogen atoms, nitro group, cyano group, alkyl groups, substituted aikyl groups, alkoxy groups, substituted alkoxy groups, groups which can be represented by $-NHCOR^8$ - (where R^8 represents an alkyl group, substituted alkyl group, phenyl group, substituted phenyl group, aralkyl group or a substituted aralkyl group), groups- which can be represented by $-NHSO_2R^8$ (where R^8 has the same meaning as before), groups which can be represented by $-SOR^8$ (where R^8 has the same meaning as before), groups which can be represented by $-SO_2R^8$ (where R^8 has the same meaning as before), groups which can be represented by $-COR^8$ (where R^8 has the same meaning as before), groups which can be represented by

$$-CON\begin{matrix} / R^9 \\ \backslash R^{10} \end{matrix}$$

(where R^9 and R^{10} may be the same or different, each representing a hydrogen . atom, alkyl group, substituted alkyl group, phenyl group, substituted phenyl group, aralkyl group or substituted alkyl group), groups which can be represented by

$$-SO_2N\begin{matrix} / R^9 \\ \backslash R^{10} \end{matrix}$$

(where R^9 and R^{10} have the same meaning as before), amino group (this may be substituted with alkyl groups), hydroxyl group and groups which fcrms a hydroxyl group by hydrolysis. In cases where there are two or more substituent groups these groups may be the same or different.

Furthermore, examples of substituent groups for the above mentioned substituted alkyl groups, substituted alkoxy groups, substituted phenyl groups and substituted aralkyl groups include hydroxyl group, nitro group, alkoxy groups which have from 1 to about 4 carbon atoms, groups which can be represented by $-NHSO_2R^8$ (where R^8 has the same significance as before), groups which can be represented by $-NHCOR^8$ (where R^8 has the same meaning as before), groups which can be represented by

$$-SO_2\begin{matrix} / R^9 \\ \backslash R^{10} \end{matrix}$$

(where R^9 and R^{10} have the same meaning as before), amino group (thismay be substituted with alkyl groups), hydroxyl group and groups which forms a hydroxy group by hydrolysis. In cases where there are two or more substituent groups these groups may be the same or different.

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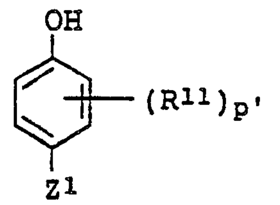
$$-SO_2\begin{matrix} / R^9 \\ \backslash R^{10} \end{matrix}$$

(Where R^9 and R^{10} have the same meaning as before), groups which can be represented by

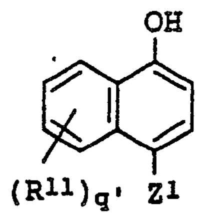
$$-CON\begin{matrix} / R^9 \\ \backslash R^{10} \end{matrix}$$

(where R^9 and R^{10} have the same meaning as before), groups which can be represented by SO_2R^8 (where R^8 has the same meaning as before), groups which can be represented by $-COR^8$ (where R^8 has the same meaning as before), halogen atoms, and amino group (this may be substituted with alkyl group).

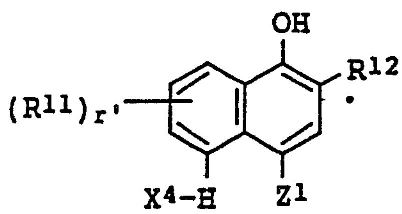
Among the coupler residual groups represented by Q in general formula [I], the phenol type compounds which can be represented by the general formulae [II] and [V] and the naphthol type compounds which can be represented by the general formulae [III] and [IV] are preferred as cyan forming couplers (these compounds loose a hydrogen atom other than the hydroxyl hydrogen atom and link-up with the $(L^1)_m(L^2)_n$ group).



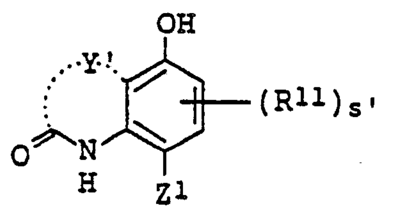
[II]



[III]



[IV]



[V]

In these formulae, R^{11} represents a group which can be substituted on a phenol ring or a naphthol ring, and examples of such groups include halogen atoms, hydroxyl group, amino group, carboxyl group, sulfo group, cyano group, aliphatic groups, aromatic groups, heterocyclic groups, carbonamido groups, sulfonamido groups, carbamoyl groups, sulfamoyl groups, ureido groups, acyloxy groups, acyl groups, aliphatic oxy groups, aliphatic thio groups, aliphatic sulfonyl groups, aromatic oxy groups, aromatic thio groups, aromatic sulfonyl groups, sulfamoylamino groups, nitro group, imido groups etc. R^{11} has from 0 to 30 carbon atoms. R^{12} represents a $-CONR^{14}R^{15}$ group, $NHCOR^{14}$ group, $-NHCOOR^{16}$ group, $-NHSO_2R^{16}$ group, $-NHCONR^{14}R^{15}$ group or $-NHSO_2R^{14}R^{15}$ group, where R^{14} and R^{15} represent hydrogen atoms, aliphatic groups which have from 1 to 30 carbon atoms (for example a methyl group, ethyl group, butyl group, methoxyethyl group, n-decyl group, n-dodecyl group, n-hexadecyl group, trifluoromethyl group, heptafluoropropyl group, dodecyloxypropyl group, 2,4-di-tert amylphenoxypropyl group, 2,4-di-tert-amylphenoxybutyl group), an aromatic group which has from 6 to 30 carbon atoms (for example a phenyl group, tolyl group, 2-tetradecyloxyphenyl group, pentafluorophenyl group, 2-chloro-5-dodecyloxycarbonylphenyl group), or a heterocyclic group which has from 2 to 30 carbon atoms (for example a 2-pyridyl group, 4-pyridyl group, 2-furyl group), and R^{16} represents an aliphatic group which has from 1 to 30 carbon atoms (for example a methyl group, ethyl group, butyl group, dodecyl group, hexadecyl group), an aromatic group which has from 6 to 30 carbon atoms (for example a phenyl group, tolyl group, 4-chlorophenyl group, naphthyl group), or a heterocyclic group (for example a 4-pyridyl group, quinolyl group, 2-furyl group). R^{14} and R^{15} may be joined together to form a heterocyclic ring (for example morpholine ring, piperidine ring, pyrrolidine ring). Moreover, p' is an integer of value 0 to 3, s' is an integer of value 0 to 2, and q' and r' are each integers of value 0 to 4.

X^4 represents an oxygen atom, a sulfur atom or an $R^{17}N<$ group, where R^{17} represents a hydrogen atom or a univalent group. Examples of univalent groups which can be represented by R^{17} include aliphatic groups which have from 1 to 30 carbon atoms (for example methyl group, ethyl group, butyl group, methoxyethyl group, benzyl group), aromatic groups which have from 6 to 30 carbon atoms (for example phenyl group, tolyl group), heterocyclic groups which have from 2 to 30 carbon atoms (for example 2-pyridyl group, 2-pyrimidyl group), carbonamido groups which have from 1 to 30 carbon atoms (for example formamido group, acetamido group, N-methylacetamido group, benzamido group), sulfonamido groups which have from 1 to 30 carbon atoms (for example methanesulfonamido group, toluenesulfonamido group, 4-chlorobenzenesulfonamido group), imido groups which have from 4 to 30 .carbon atoms (for example succinimido group), and groups which can be represented by $-OR^{18}$, SR^{18}, $-COR^{18}$, $-CONR^{18}R^{19}$, $-COCOR^{18}$, $-COCONR^{18}R^{19}$, $-COOR^{20}$, $-COCOOR^{20}$, $-SO_2R^{20}$, SO_2OR^{20}, $SO_2NR^{18}R^{19}$ and $-NR^{18}R^{19}$. Here, R^{18} and R^{19} may be the same or different, each representing a hydrogen atom, an aliphatic group which has from 1 to 30 carbon atoms (for example methyl group, ethyl group, butyl group, dodecyl group, methoxyethyl group, trifluoromethyl group, pentafluoropropyl group), an aromatic group which has from 6 to 30 carbon atoms (for example phenyl group, tolyl group, 4-chlorophenyl group, pentafluorophenyl group, 4-cyanophenyl group, 4-hydroxyphenyl group) or a heterocyclic group which has from 2 to 30 carbon atoms (for example 4-pyridyl group, 3-pyridyl group, 2-furyl group). R^{18} and R^{19} may be joined together to form a heterocyclic group (for example a morpholino group, pyrrolidino group).

R^{20} can represent any of the substituent groups indicated as examples of R^{18} and R^{19} except the hydrogen atom.

Z^1 represents a hydrogen atom or a group which can be eliminated by a coupling reaction with the oxidized form of a primary aromatic amine. Examples of groups which can be eliminated include halogen atoms (for example fluorine atom, chlorine atom, bromine atom, iodine atom), aliphatic oxy groups which have from 1 to 30 carbon atoms (for example methoxy group, ethoxy group, 2-hydroxyethoxy group, carboxymethyloxy group, 3-carboxypropyloxy group, 2-methoxyethoxycarbamoylmethyloxy group, 2-methanesulfonylethoxy group, 2-carboxymethylthioethoxy group, triazolylmethyloxy group), aromatic oxy groups which have from 6 to 30 carbon atoms (for example phenoxy group, 4-hydroxyphenoxy group, 2-acetamidophenoxy group, 2,4-dibenzenesulfonamidophenoxy group, 4-phenylazophenoxy group), heterocyclic oxy groups which have from 2 to 30 carbon atoms (for example 4-pyridyloxy group, 1-phenyl-5-tetrazolyloxy group), aliphatic thio groups which have from 1 to 30 carbon atoms (for example dodecylthio group), aromatic thio groups which have from 6 to 30 carbon atoms (for example 4-dodecylphenylthio group), heterocyclic thio groups which have from 2 to 30 carbon atoms (for example 4-pyridylthio group, 1-phenyltetrazol-5-ylthio group), acyloxy groups which have from 2 to 30 carbon atoms (for example acetoxy group, benzoyloxy group, lauroyloxy group), carbonamido groups which have from 1 to 30 carbon atoms (for example dichloroacetylamido group, trifluoroacetamido group, heptafluorobutanamido group, pentafluorobenzamido group), sulfonamido groups which have from 1 to 30 carbon atoms (for example methanesulfonamido group, ethanesulfonamido group), aromatic azo groups which have from 6 to 30 carbon atoms (for example phenylazo group, 4-chlrophenylazo group, 4-methoxyphenylazo group, 4 pivaloylaminophenylazo group), aliphatic oxycarbonyloxy groups which have from 2 to 30 carbon atoms (for example ethoxycarbonyloxy group, dodecyloxycarbonyloxy group), aromatic oxycarbonyloxy groups which have from 7 to 30 carbon atoms (for example phenoxycarbonyloxy group), carbamoyloxy groups which have from 1 to 30 carbon atoms (for example methylcarbamoyloxy group, dodecylcarbamoyloxy group, phenylcarbamoyloxy group), and heterocyclic groups which have from 1 to 30 carbon atoms and which are linked to the active site of the coupler with a nitrogen atom (for example succinimido group, phthalimido group, hydantoinyl group, pyrazolyl group, 2 benzothrozolyl group).

Y′ Represents a group of atoms which is required to form, together with the carbon atoms to which it is bound, a five to seven membered ring. Actual example include -O-,

$-N(R^7)-$, $-C(=O)-$, $-S-$, $-N=$, $=N-$, $-C(R'')=$, $=C(R'')-$ and

$-C(R'')(R''')-$,

and combinations of these groups. R″ and R‴ each independently represent a hydrogen atom, alkyl group, aryl roup, halogen atom, alkoxy group, alkoxycarbonyl group, arylcarbonyl group, alkylcarbamoyl group, arylcarbamoyl group or a cyano group.

Examples of the substituent groups preferably used in the invention are indicated below.

The preferred substituents represented by R^{11} are Lalogen atoms (for example fluorine, chlorine, bromi e etc.), aliphatic groups (for example methyl group, ethyl group, isopropyl group), carbonamido groups (for example acetamido group, benzamido group), sulfonamido groups (for example methanesulfonamido group toluenesulfonamido group).

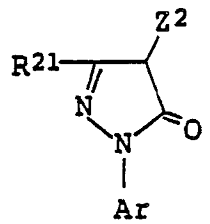
The groups represented by $-CONR^{14}R^{15}$ are preferred fo R^{12}, and examples include carbamoyl group, ethyl carbamoyl group, morpholinocarbamoyl group, dodecylcarbamoyl group, hexadecylcarbamoyl group, decylcarbamoyl group, decyloxypropyl group, dodecyloxypropyl group, 2,4-di-tert-amylphenoxypropyl group and 2,4-ditert-amylphenoxybutyl group.

$R^{17}N<$ is preferred for X^4, and even more desiiable for R^{17} are the $-COR^{18}$ group (for example formyl group, acetyl group, trifluoroacetyl group, chloroacetyl group, benzoyl group, pentafluorobenzoyl group, pchlorobenzoyl group), the $-COOR^{20}$ group (for example methoxycarbonyl group, ethoxycarbcnyl group, butoxycarbonyl group, dodecyloxycarbonyl group, methoxyethoxycarbonyl group, phenoxycarbonyl group), the $-SO_2R^{20}$ group (for example methanesulfonyl group, ethanesulfonyl group, butanesulfonyl group, hexadecanesulfonyl group, benzenesulfonyl group, toluenesulfonyl group, p-chlorobenzenesulfonyl group), the $-CONR^{18}R^{19}$ group (N,Ndimethylcarbamoyl group, N,N-diethylcarbamoyl group, N,N-dibutylcarbamoyl group, morpholinocarbonyl group, piperidinocarbonyl. group, 4-cyanophenylcarbamoyl group, 3,4-dichlorophenylcarbamoyl group, 4-methanesulfonylphenylcarbamoyl group), and the $SO_2NR^{18}R^{19}$ group (for example N,N-dimethylsulfamoyl group, N,N-diethylsulfamoyl group, N,N-dipropylsulfamoyl group). Among these groups, the $-COR^{18}$ group, $-COOR^{20}$ group and the $-SO_2R^{20}$ group are especially desirable for R^{17}.

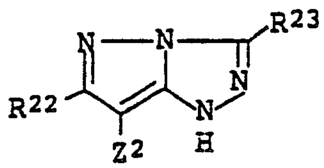
The preferred groups for Z^1 are the hydrogen atom, the halogen atoms, the aliphatic oxy groups, the aromatic oxy groups, the heterocyclic thio groups and the aromatic azo groups.

Couplers which can be represented by the general formulae [II]-[V] may consist of dimers or larger oligomers which are bonded together via linking groups which have a valency of two or more by means of the substituent groups R^{11}, R^{12}, X^4 or Z^1. In such Cases the groups are not limited to the numbers of carbon atoms shown for each of the aforementioned substituent groups (linked by $-(L^1)_m-(L^2)_n-$ in any of Ar, Z^2).

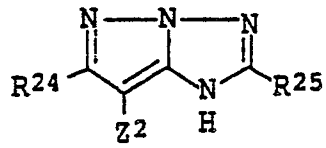
Among the sample residual groups represented by Q in general formula [I], coupler residual groups which can be represented by the general formulae [VI], [VII], [VIII], [IX], [X], [XI] and [XII] are preferred as magenta color forming coupler residual groups (linked by $-(L^1)_m-(L^2)_n-$ in any of Ar, Z^2, R^{21} to R^{33}). In the case of general formula [VI], it is preferred that there is direct linking at the position of the R^{21} substituent.



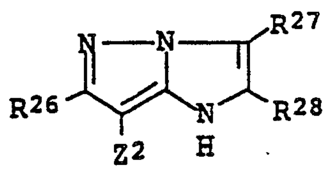
[VI]



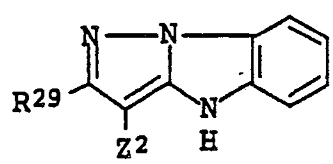
[VII]



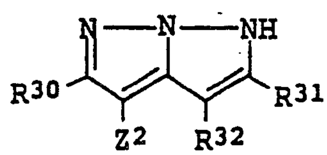
[VIII]



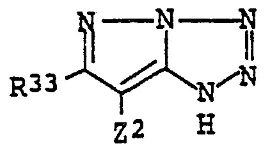
[IX]



[X]



[XI]



[XII]

In these formulae, Ar represents a substituent group of the known type in the 1-position of a 2-pyrazolin-5-one coupler, for example an alkyl group, substituted alkyl group (for example a haloalkyl group such as a fluoroalkyl group, acylalkyl group, benzylalkyl group), an aryl group or substituted aryl group with, as substituent groups, alkyl groups (for example methyl group, ethyl group), alkoxy groups (for example methoxy group, ethoxy group), aryloxy groups (for example phenyloxy group), alkoxycarbonyl groups (for example methoxycarbonyl group), acylamino groups (for example acetylamino group), carbamoyl groups, alkylcarbamoyl groups (for example methylcarbamoyl group, ethylcarbamoyl group), dialkylcarbamoyl groups (for example dimethylcarbamoyl group, arylcarbamoyl groups (for example phenylcarbamoyl group, alkylsulfonyl groups (for example methylsulfonyl group), arylsulfonyl groups (for example phenylsulfonyl group), alkylsulfonamido groups (for example methanesulfonamido group), arylsulfonamido groups (for example phenylsulfonamido group), sulfamoyl groups, alkylsulfamoyl groups (for example ethylsulfamoyl group), dialkyl sulfamoyl groups (for example dimethylsulfamoyl group), alkylthio groups (for example methylthio group), cyano groups, nitro groups, halogen atoms (for example fluorine atom, chlorine atom, bromine atom), and in cases where there are two or more substituent groups these may be the same or different. The preferred substituent groups are halogen atoms, alkyl groups, alkoxy groups, alkoxycarbonyl groups and cyano groups.], or a heterocyclic group (for example triazole, thiazole, benzthiazole, furan, pyridine, quinaldine, benzoxazole, pyrimidine, oxazole, imidazole).

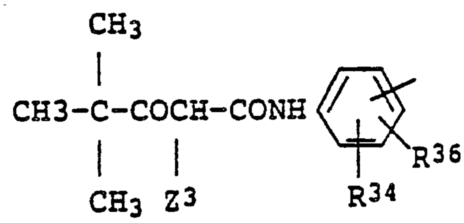
R^{21} represents an unsubstituted anilino group, an acylamino group (for example an alkylcarbonamido group, phenylcarbonamido group, alkoxycarbonamido group, phenyloxycarbonamido group), or a ureido group (for example an alkylureido group, phenylureido group), and these groups may have, as substituent groups, halogen atoms (for example fluorine atoms, chlorine atoms, bromine atoms), linear chain or branched alkyl groups (for example methyl group, t-butyl group, octyl group, tetradecyl- group), alkoxy groups (for example methoxy group, ethoxy group, 2-ethylhexyloxy group, tetradecyloxy group), acylamino groups (for example acetamido group, benzamido group, butanamido group, octanamido group, tetradecanamido group, α-(2,4-di-tert amylphenoxy)acetamido group, α-(2,4-di-tert-amylphenoxy)butylamido group, α-(3-pentadecylphenoxy)hexanamido group, α-(4-hydroxy-3-tert-butylphenoxy)tetradecanamido group, 2-oxo-pyrrolidin-1-yl group, 2-oxo-5-tetradecylpyrrolidin-1-yl group, N-methyltetradecanamido group), sulfonamido groups (for example methanesulfonamido group, benzenesulfonamido group, ethanesulfonamido group, p-toluenesulfonamido group, octanesulfonamido group, p-toluenesulfonamido group, N-methyl-tetradecanesulfonamido group), sulfamoyl groups (for example sulfamoyl group, N-methylsulfamoyl group, N-ethylsulfamoyl group, N,N-dimethylsulfamoyl group, N,N-dihexylsulfamoyl group, N-hexadecylsulfamoyl group, N-[3-(dodecyloxy)propyl]sulfamoyl group, N-[4-(2,4-di tertamylphenoxy)butyl]sulfamoyl group, N-metnyl-N-tetradecylsulfamoyl group.), carbamoyl groups (for example N-methylcarbamoyl group, N butylcarbamoyl group, N-octadecylcarbamoyl group, N-[4-(2,4-di-tert-amylphenyl)butyl]carbamoyl group, N-methyl-N-tetradecylbutylcarbamoyl group, N-methyl-N-tetradecylcarbamoyl group), diacylamino groups (N-succinimido group, N-phthalimido group, 2,5-dioxo-1-oxazolidinyl group, 3-dodecyl-2,5-dioxo-1-hydantoinyl group, 3-(N-octyl-N-dodecylamino)succinimido group), alkoxycarbonyl groups (for example methoxycarbonyl group, tetradecyloxy carbonyl group, benzyloxvcarbo.nyl group), alkoxysulfonyl groups (for example methoxysulfonyl group, butoxysulfonyl group, octyloxysulfonyl group, tetradecyloxysulfonyl group}, aryloxysulfonyl groups (for example phenoxysulfonyl group, p-methylphenoxysulfonyl group, 2,4-di-tert-amylphenoxysulfonyl group), alkanesulfonyl groups (for example methanesulfonyl group, ethanesulfonyl group, octanesulfonyl group, 2-ethylhexylsulfonyl group, hexadecanesulfonyl group), arylsulfonyl grouos. (for example benzenesulfonyl group, 4-nonylbenzenesulfonyl group), alkylthio groups (for example methylthio group, ethylthio group, hexylthio group, benzylthio group, tetradecylthio group, 2-(2,4-di-tert-amylphenoxy)ethylthio group), arylthio groups (for example phenylthio group, p-tolylthio group), alkyloxycarbonylamino groups (for example methoxycarbonylamino group, ethyloxycarbonylamino group, benzyloxycarbonylamino group, hexadecyloxycarbonylamino group), alkylureido groups (for example N-methylureido group, N,N-dimethylureido group, N-methyl-N-dodecylureido group, N-hexadecylureido group, N,N-dioctadecylureido group), acyl groups (for example acetyl group, benzoyl group, octadecanoyl group, p-dodecanamido benzoyl group), nitro groups, carboxyl groups, sulfo groups, hydroxyl groups or trichloromethyl groups.

However, the number of carbon atoms in those of the above mentioned substituent groups designated as alkyl groups is from 1 to 36 and the number of carbon atoms in those groups designated as aryl groups is from 6 to 38.

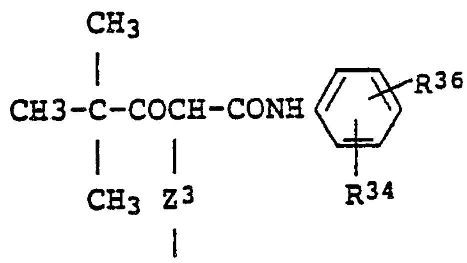
R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}, R^{28}, R^{29}, R^{30}, R^{31}, R^{32} and R^{33} each represents a hydrogen atom or a hydroxyl group, or they may each represent an unsubstituted or a substituted alkyl group (for example an alkyl group which has from 1 to 20 carbon atoms, such as a methyl group, propyl group, t-butyl group, trifluoromethyl group, tridecyl group etc.), an aryl group (for example an aryl group which has from 6 to 20 carbon atoms, such as a phenyl group, 4-t-butylphenyl group, 2,4-di-t-amylphenyl group, 4-methoxyphenyl group), a heterocyclic group (for example a 2 furyl group, 2-thienyl group, 2-pyrimidyl group, 2-benzothiazolyl group), an alkylamino group (for example an alkylamino group which has from 1 to 20 carbon atoms, such as a methylamino group, diethylamino group, t-butylamino group, an acylamino group (for example an acylamino group which has from 2 to 20 carbon atoms, such as an acetylamino group, propylamino group, benzamido group), an anilino group (for example a phenylamino group, 2-chloroanilino group), an alkoxycarbonyl group (preferably an alkoxy carbonyl group which has from 2 to 20 carbon atoms, such as a methoxycarbonyl group, butoxycarbonyl group, 2-ethylhexyloxycarbonyl group), an alkylcarbonyl group (preferably an alkylcarbonyl group which has from 2 to 20 carbon atoms, such as an acetyl group, butylcarbonyl group, cyclohexylcarbonyl group), an arylcarbonyl group (preferably an arylcarbonyl group which has from 7 to 20 carbon atoms, such as a benzoyl group, 4-t-butylbenzoyl group), an alkylthio group (preferably an alkylthio group which has from 1 to 20 carbon atoms, such as a methylthio group, octylthio group, 2-phenoxyethylthio group), an arylthio group (preferably an arylthio group which has from 6 to 20 carbon atoms, such as a phenylthio group, 2-butoxy-5-t-octylphenylthio group), a carbamoyl group (preferably a carbamoyl group which has from 1 to 20 carbon atoms, such as an N-ethylcarbamoyl group, N,N-dibutylcarbamoyl group, N-methyl-N-butylcarbamoyl group), a sulfamoyl group (preferably a sulfamoyl group which has up to 20 carbon atoms, such as an N-ethylsulfamoyl group, N,N-diethylsulfamoyl group, N,N-dipropylsulfamoyl group), or a sulfonamido group (preferably a sulfonamido group which has from 1 to 20 carbon atoms, such as a methanesulfonamido group, benzenesulfonamido group, p-toluenesulfonamido group).

Z^2 represents a hydrogen atom or a group which can be eliminated by a coupling reaction with the oxidized form of a primary aromatic amine developing agent. The group which can be eliminated can be a halogen atom (for example a chlorine atom, bromine atom), a coupling elimination group which is linked with an oxygen atom (for example an acetoxy group, propanoyloxy group, benzoyloxy group, ethoxyoxaloyloxy group, pyruvinyloxy group, cinnamoyloxy group, phenoxy group, 4-cyanophenoxy group, 4-methanesulfonamidoohenoxy group, c-naphthoxy group, 3-pentadecylphenoxy group, benzyloxycarbonyloxy group, ethoxy group, 2-cyanoethoxy group, benzoyloxy group, 2-phenethyloxy group, 2-phenoxyethoxy group, 5-phenyltetrazolyloxy group, 2-benzothiazolyloxy group), a coupling elimination group which is linked with a nitrogen atom (for example those disclosed in JP-A-59-99437 [the term "JP-A" as used herein signifies an unexamined published Japanese patent application], and actual examples include benzenesulfonamido group, N-ethyltoluenesulfonamido group, heptafluorobutanamido group, 2,3,4,5,6-pentafluorobenzamido group, octanesulfonamido group, p-cyanophenylureido group, N,N-diethylsulfamoylamino group, 1-piperidyl group, 5,5-dimethyl-2,4 dioxo-3-oxazolidinyl group, 1-benzyl-5-ethoxy-3-hydantoinyl group, 2-oxo-1,2-dihydro- 1-pyridinyl group, imidazolyl group, pyrazolyl group, 3,5-diethyl-1,2,4-triazol-1-yl group, 5- or 6-bromobenzotriazol-1-yl group, 5-methyl-1,2,3,4-tetrazol-1-yl group, benzimidazolyl group), or a coupling elimination group which is linked with a sulfur atom (for example a phenylthio group, 2-carboxyphenylthio group, 2-methoxy-5-octylphenylthio group, 4-methanesulfonylphenylthio group, 4-octanesulfonamidophenylthio group, benzylthio group, 2 cyanoethylthio group, 5-phenyl-2,3,4,5-tetrazolylthio group, 2 benzothiazolyl group). The group which can be eliminated is preferably a halogen atom, a coupling elimination group which is linked with an oxygen atom or a coupling elimination group which is linked with a nitrogen atom, and it is most desirably an alkyloxy group, a chlorine atom, a pyrazolyl group, an imidazolyl group or a triazolyl group.

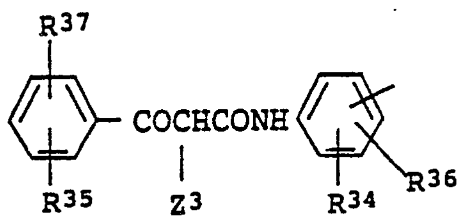
Among the coupler residual groups represented by Q in general formula [I], coupler residual group is preferably of the acylacetamide type, and those of the pivaloylacetanilide type which can be represented by the general formulae [XIII] and [XIII′] and those of the benzoylacetanilide type which can be represented by the general formulae [XIV], [XIV′], [XV] and [XV′] are especially preferred as yellow color forming coupler residual groups (the free bonds shown in the general formulae are linked to the $-(L^1)_m-(L^2)_n-$ group.



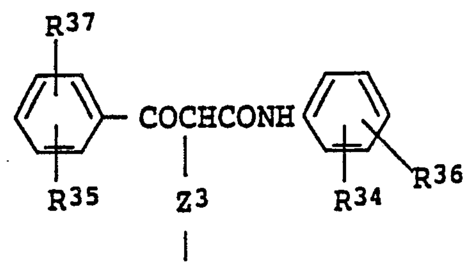
[XIII]



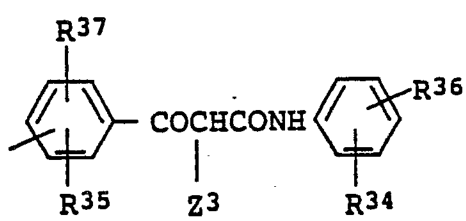
[XIII']



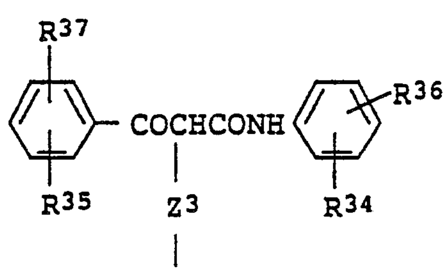
[XIV]



[XIV']



[XV]



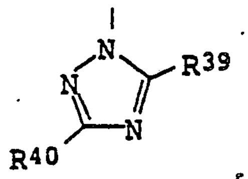
[XV']

In these formulae, R^{34}, R^{35}, R^{36} and R^{37} each represent a hydrogen atom or a known substituent group for a yellow color forming coupler residual group, for example an alkyl group, alkenyl group, alkoxy group, alkoxycarbonyl group, halogen atom, alkoxycarbamoyl group, aliphatic amido group, alkylsulfamoyl group, alkylsulfonamido group, alkylureido group, alkyl substituted succinimido group, aryloxy group, aryloxycarbonyl group, arylcarbamoyl group, arylamido group, arylsulfamoyl group, arylsulfonamido group, arylureido group, carboxyl group, sulfo group, nitro group, cyano group, thiocyano group, and these substituent groups may be the same or different.

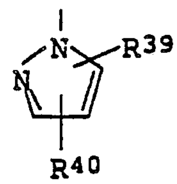
Z^3 is a hydrogen atom or a group which can be represented by the general formulae [XVI], [XVII], [XVIII] or [XIX] as indicated below.

$-OR^{38}$ [XVI]

Here R^{38} represents a heterocyclic group or an alkyl group which may be substituted.

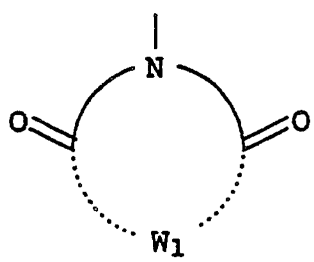


[XVI]



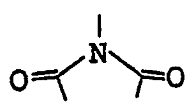
[XVII]

R^{39} and R^{40} each represents a hydrogen atom, halogen atom, carboxylic acid ester group, amino group, alkyl group, alkylthio group, alkoxy group, alkylsulfonyl group, alkylsulfinyl group, carboxylic acid group, sulfonic acid group, unsubstituted or substituted phenyl group or a heterocyclic group, and these groups may be the same or different.



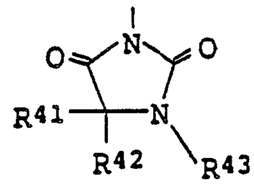
[XIX]

W_1 is a group of non-metal atoms required to form a four, five or six membered ring together with the

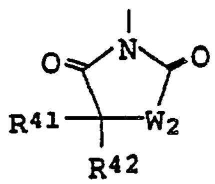


part shown in the formula.

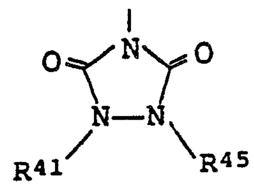
Of the compounds represented by the general formula [XIX], those which can also be represented by the general formulae [XX] to [XXII] are preferred.



[XX]



[XXI]

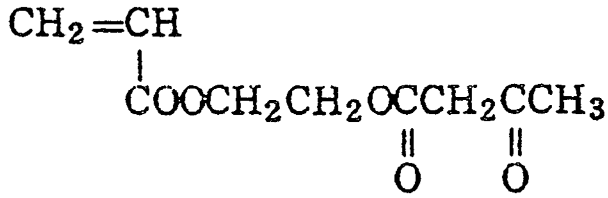


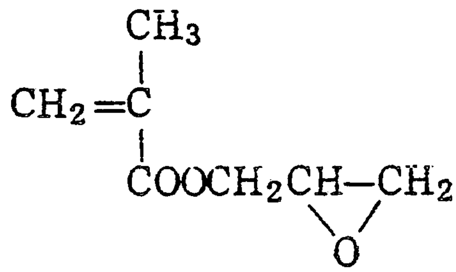
[XXII]

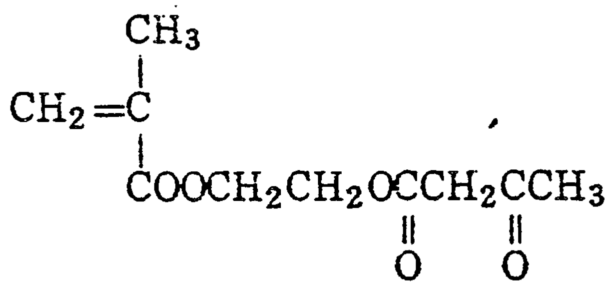
In these formulae, R^{41} and R^{42} each represents a hydrogen atom, alkyl group, aryl group, alkoxy group, aryloxy group or a hydroxyl group, R^{43}, R^{44} and R^{45} each represents a hydrogen atom, alkyl group, aryl group, aralkyl group or an acyl group, and W_2 represents an oxygen atom or a sulfur atom.

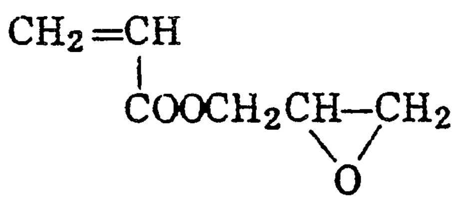
Preferred examples of the ethylenic unsaturated monomers which provide the repeating units represented by B include acrylic acid, α-chloroacrylic acid, α-alkylacrylic acids (for example methacrylic acid), esters and amides derived from these acids (for example acrylamide, methacrylamide, n-butylacrylamide, t-butylacrylamide, 2-methoxyethylacrylamide, diacetoneacryl amide, 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, cyclohexyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate), β-alkoxyethyl (meth)acrylates (for example 2-ethoxyethyl acrylate, 2-methoxymethyl methacrylate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, 2-ethoxymethyl methacrylate, 2-butoxyethyl acrylate, 2-n-butyloxyethyl acrylate, 2-(2-methoxyethoxyethyl acrylate), β-sulfonamidoethyl (meth)acrylate, β--carbonamidoethyl (meth)acrylate, β--alkoxyethylacrylamide (the alkoxy group may also contain a plurality of substituted alkoxy groups), β-sulfonamidoethylacrylamide, β-carbonamidoethylacrylamide), vinyl esters (for example vinyl acetate, vinyl laurate), acrylonitrile, methacrylonitrile, dienes (for example butadiene, isoprene), aromatic vinyl compounds (for example styrene, divinyl benzene and derivatives thereof, for example vinyltoluene, vinylacetophenone and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers (for example vinyl ethyl ether), maleic anhydride, maleic acid esters, N-vinyl-2- pyrrolidone, N-vinylpyridine and 2- and 4-vinyl pyridine, ethylene, propylene, 1-butene, isobutene etc.

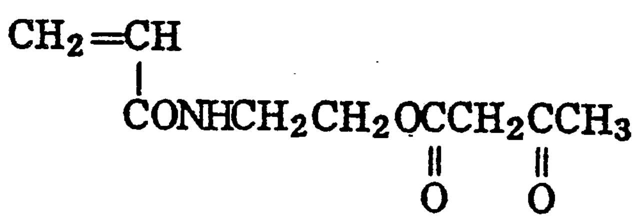
Furthermore, B may be a repeating unit derived from an ethylenically unsaturated monomer which binds directly, or via a film hardening agent, with the binder of the layer in which the polymeric coupler is present. Ethylenically unsaturated monomers of this type are indicated below:







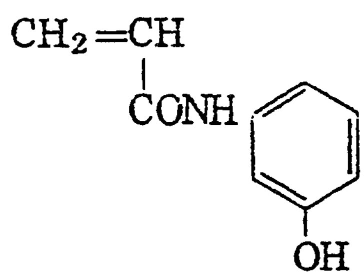


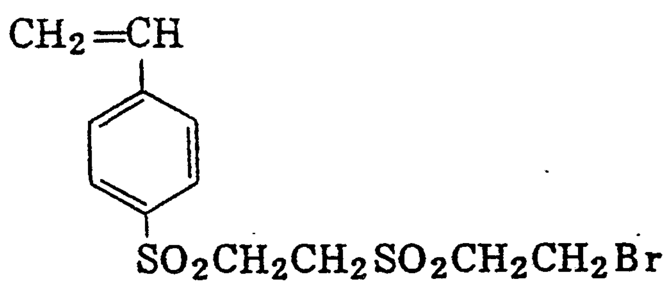


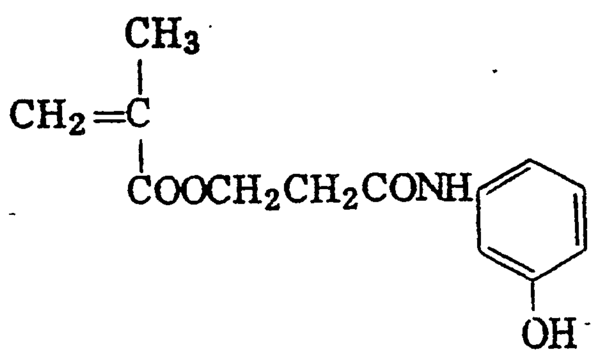
$$CH_2{=}CH{-}CONHCH_2NHCOCH_2CH_2SO_2CH_2CH_2Cl$$

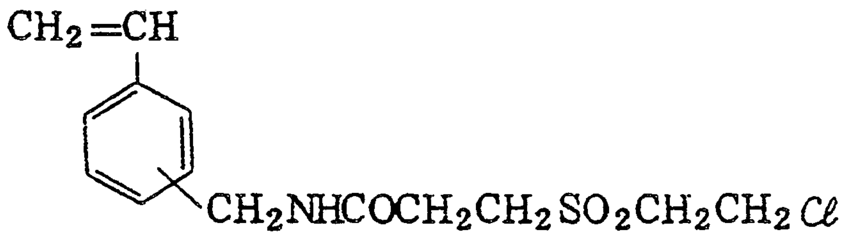
$$CH_2{=}C(CH_3){-}CONHCH_2CH_2OC({=}O)CH_2C({=}O)CH_3$$

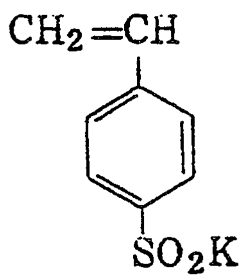
$$CH_2{=}CH{-}CO_2CH_2CH_2OCOCH_2CH_2SO_2CH_2CH_2Cl$$

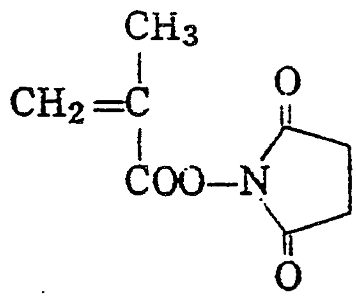


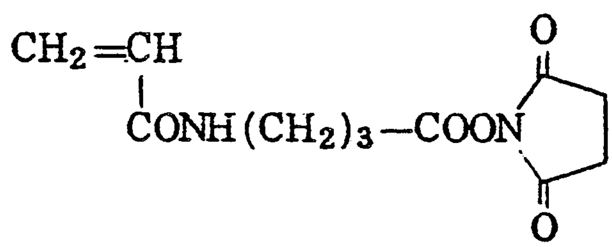


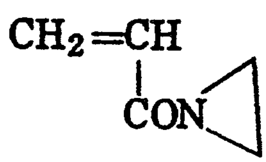


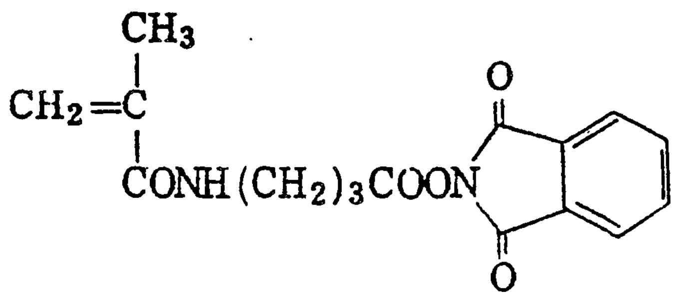


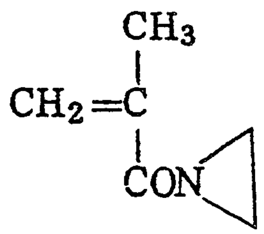


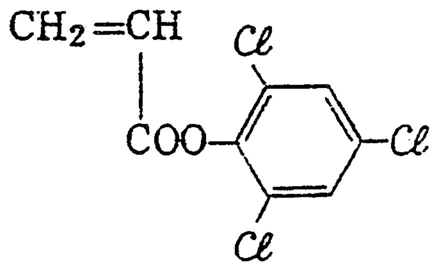


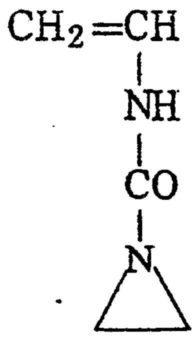


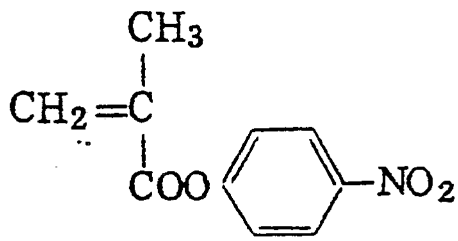


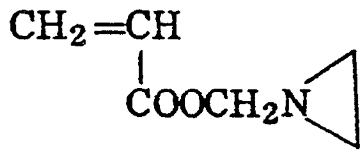


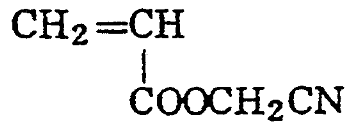


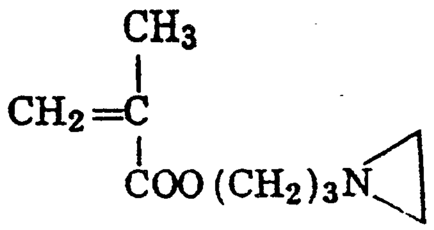


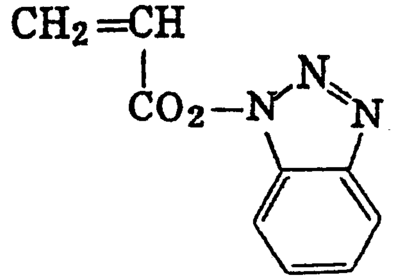










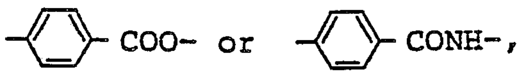


Two or more types of ethylenically unsaturated monomer can be used conjointly.

For example, use can be made of ethyl acrylate and n-butyl acrylate, n-butylacrylate and styrene, n-butylacrylate and t-butylacrylamide, 2-methoxymethyl methacrylate and potassium styrenesulfinate, etc.

Especially desirable components represented by the general formula [I] are those in which the individual substituents have the following meanings.

R^1 represents a hydrogen atom or a methyl group, Ll represents -CONH, -COO-, -OCO-,



m represents 1, and n represents 0 or 1. L^2 can be represented by: $\{X^1\{J^1\text{-}X^2)_p\{J^2\text{-}X^3)_q\{J^3)_r\}_s$

In the preferred cases J^1, J^2 and J^3 may be the same or different, each representing -CO-, $-SO_2-$, -CONH-, $-SO_2NH-$, -NHCO-, $-NHSO_2$, -O-, -NHCONH-, -S-, -COO-, -OCO-, -NHCOO- or -OCONH; X^1, X^2 and X^3 may be the same or different, each representing an alkylene group (which has from 1 to 4 carbon atoms), an arylene group, or a substituted arylene group, and p, q, r and s each represent 0 or 1.

Of these possibilities, the acrylic acid esters, methacrylic acid esters, acrylamides, methacrylamides, maleic acid esters, styrenes, and ethylenic monomers which can bind directly or via a film hardening agent with the binder are the most desirable for B.

In the aforementioned general formula [P], E represents a univalent group which has at least 8 carbon atoms and which originates from the radical part which is formed by chain transfer to a chain transfer agent of which the chain transfer constant for a monomeric coupler is at least 0.1 but not more than 20, and it can, for example, be represented by the general formula [XXII].

General Formula [XXII]

$E^1\{Y\}_p$

Thus, E^1 may be an alkyl group, substituted alkyl group, substituted aryl group, or substituted naphthyl group etc., which has at least 8 carbon atoms.

These groups may be further substituted, and examples of substituents group include halogen atoms, cyano group, alkyl groups, substituted alkyl groups, alkoxy groups, substituted alkoxy groups, $-NHCOR^{46}$ groups where R^{46} represents an alkyl group, substituted alkyl group, phenyl group, substituted phenyl group or an aralkyl group), $-NHSO_2R^{46}$ groups (where R^{46} has the same significance as described above), $-OCOR^{46}$ groups (where R^{46} has the same meaning as described above), $-SOR^{46}$ groups (where R^{46} has the same meaning as described above),

$$-CON(R^{47})R^{48}$$

groups (where R^{47} and R^{48} may be the same or different, each representing a hydrogen atom, alkyl group, substituted alkyl group, phenyl group, substituted phenyl group, aralkyl group, or a substituted aralkyl group),

$$-SO_2N(R^{47})R^{48}$$

groups (where R^{47} and R^{48} have the same meaning as described above), amino group, (this may be substituted with alkyl groups), hydroxyl group and groups which form a hydroxyl group by hydrolysis.

Furthermore, examples of substituent groups for the abovementioned alkyl groups, substituted alkoxy groups and substituted aralkyl groups include hydroxyl group, alkoxy groups which have from 1 to about 4 carbon atoms, $-NHSO_2R^{46}$ groups (where R^{46} has the same meaning as described above), $NHCOR^{46}$ groups (where R^{46} has the same meaning as described above), $-COOR^{46}$ groups (where R^{46} has the same meaning as described above), $-OCOR^{46}6$ groups (where R^{46} has the same meaning as described above),

$$-SO_2N\begin{matrix} R^{47} \\ R^{48} \end{matrix}$$

groups (where R^{47} and R^{48} have the same meaning as described above,

$$-CON\begin{matrix} R^{47} \\ R^{48} \end{matrix}$$

groups (where R^{47} and R^{48} have the same meaning as described above), $-SO_2R^{46}$ groups (where R^{46} has the same significance as described above), halogen atoms, cyano group, and amino group (which may be substituted with alkyl groups).

Preferred examples of E^1 are indicated below, but E^1 is not limited to these groups.

$C_8H_{17}-$ $C_{10}H_{21}-$, $C_{12}H_{25}-$,

$C_{14}H_{29}$, $C_{15}H_{31}-$, $C_{16}H_{33}-$,

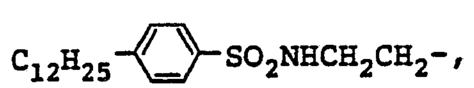
$C_{18}H_{37}-$, $C_{20}H_{41}-$, $C_{31}H_{63}-$,

$C_8H_{17}OC(=O)CH_2-$, $C_{12}H_{25}OC(=O)CH_2-$,

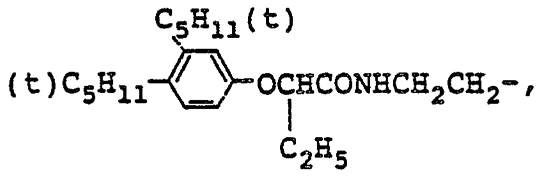
$C_{18}H_{37}OC(=O)CH_2-$, $C_2H_5OC(=O)CHC_{12}H_{25}$,

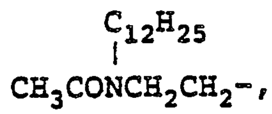
$C_{12}H_{25}OC(=O)CH_2CH_2-$, $C_{18}H_{37}OC(=O)CH_2CH_2-$,

$C_{16}H_{33}SO_2NHCH_2CH_2-$,



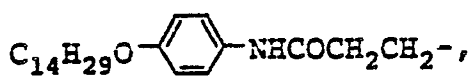
$C_8H_{17}CONHCH_2CH_2-$, $C_{13}H_{27}CONHCH_2CH_2-$, $C_{15}H_{31}CONHCH_2CH_2-$, $C_{17}H_{35}CONHCH_2CH_2-$,

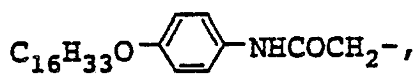


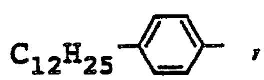


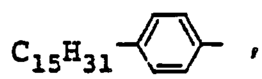
$C_{12}H_{25}NHCH_2CH_2$-,

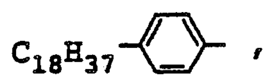
$C_{16}H_{33}NHCH_2CH_2$-, $C_{12}H_{25}NHCOCH_2$-, $C_{18}H_{37}NHCOCH_2$-,

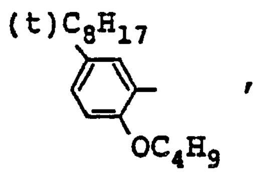


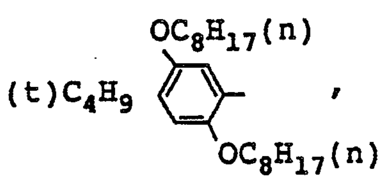


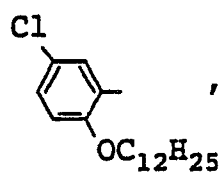


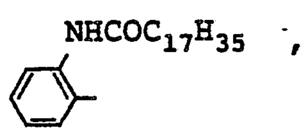


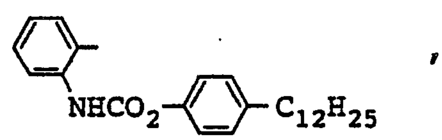


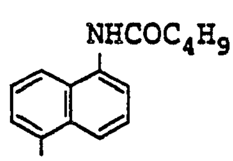












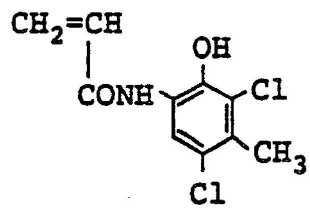
In general formula [XXII], Y represents -S-, -SO- or $-SO_2$-, and p represents 0 or 1.

In general formula [P], X preferably represents a hydrogen atom or a halogen atom (fluorine atom, chlorine atom, bromine atom, iodine atom).

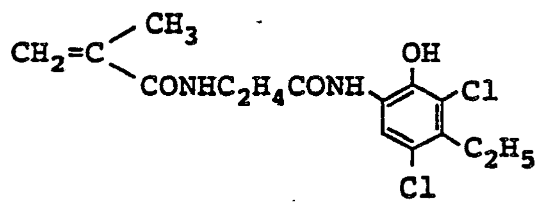
Typical examples of the monomeric couplers which provide coupler units which have a coupler residual group which can couple with a primary aromatic amine developing agent and form a dye, and which can be represented by the general formula [I] which is the color forming part, are indicated below, but the invention is not limited to these examples.

Furthermore, the monomeric couplers may be used individually or a plurality of monomeric couplers can be used.

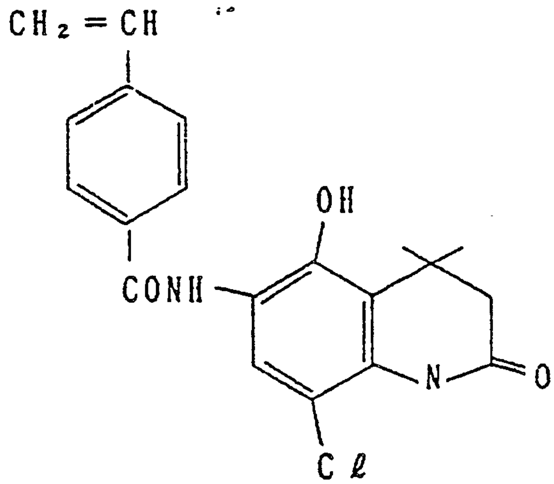
(1)



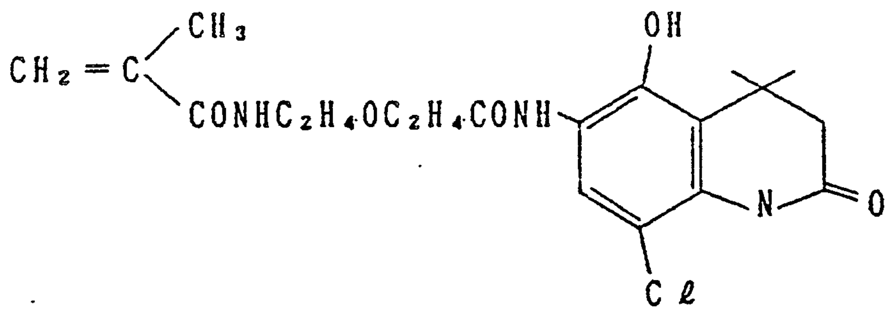
(2)



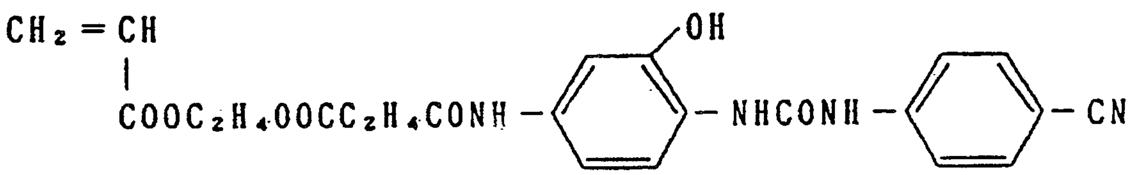
(3)



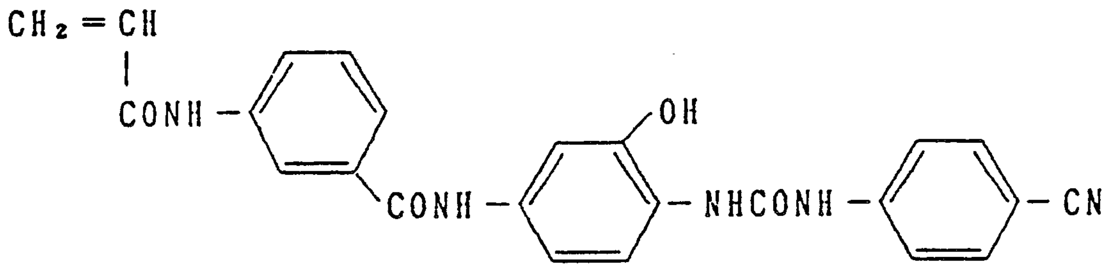
(4)



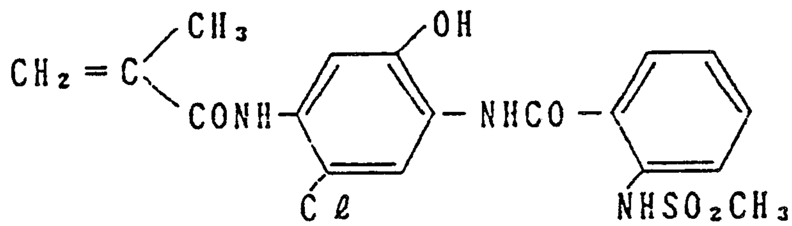
(5)



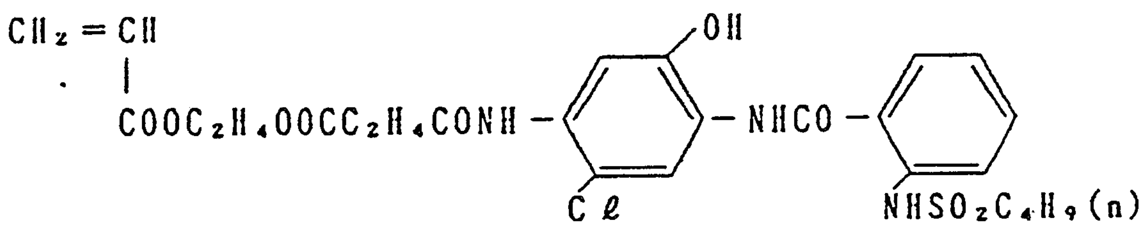
(6)


CH₂ = CH
CONH
OH
CONH
NHCONH
CN

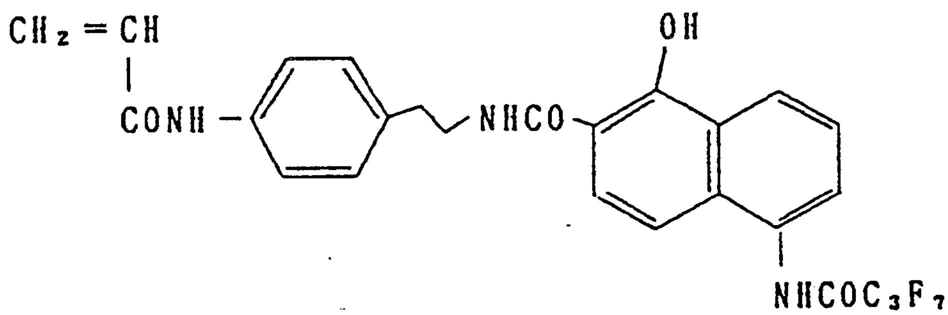
(7)


CH₃
OH
CH₂ = C
CONH
NHCO
Cℓ
NHSO₂CH₃

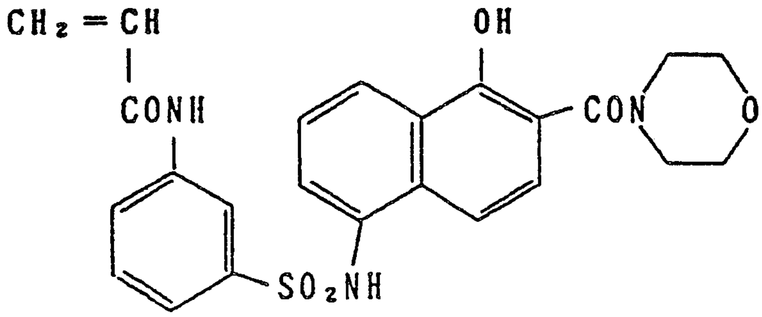
(8)


CH₂ = CH
OH
COOC₂H₄OOCC₂H₄CONH
NHCO
Cℓ
NHSO₂C₄H₉(n)

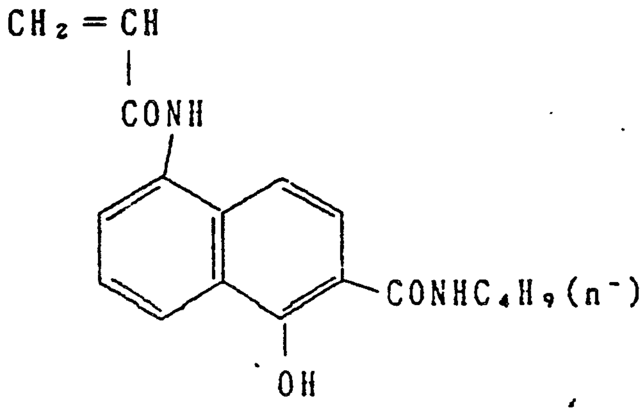
(9)


CH₂ = CH
OH
CONH
NHCO
NHCOC₃F₇

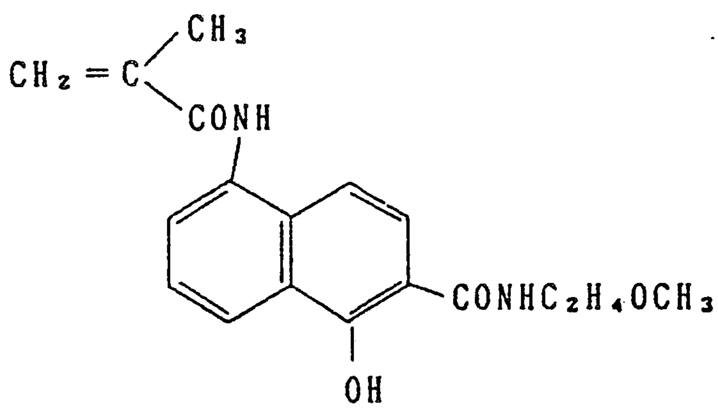
(10)



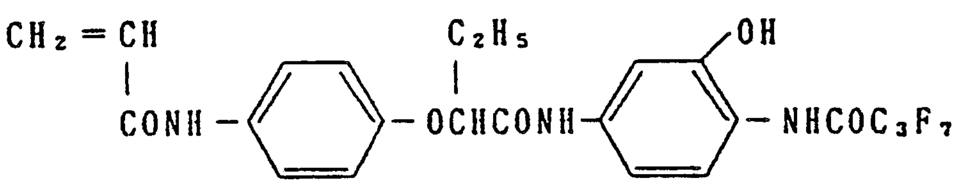
(11)



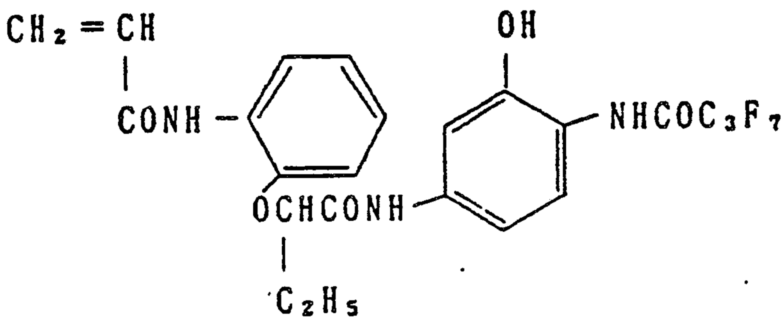
(12)



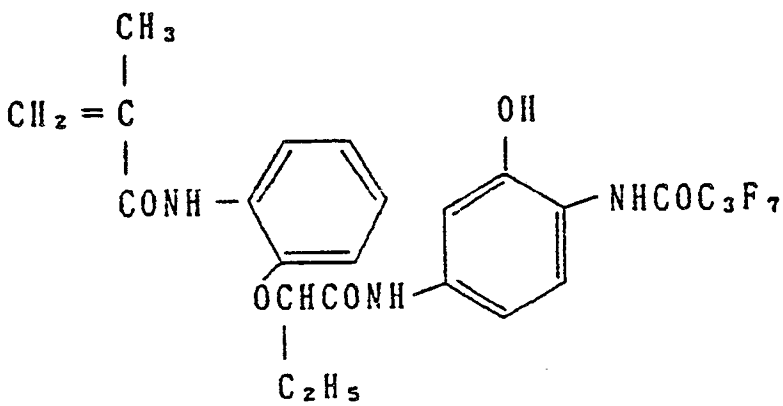
(13)



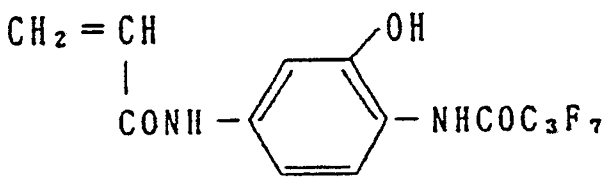
(14)


CH₂=CH
CONH
OH
NHCOC₃F₇
OCHCONH
C₂H₅

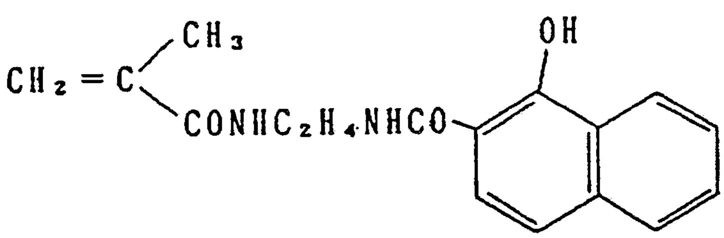
(15)


CH₃
CH₂=C
CONH
OH
NHCOC₃F₇
OCHCONH
C₂H₅

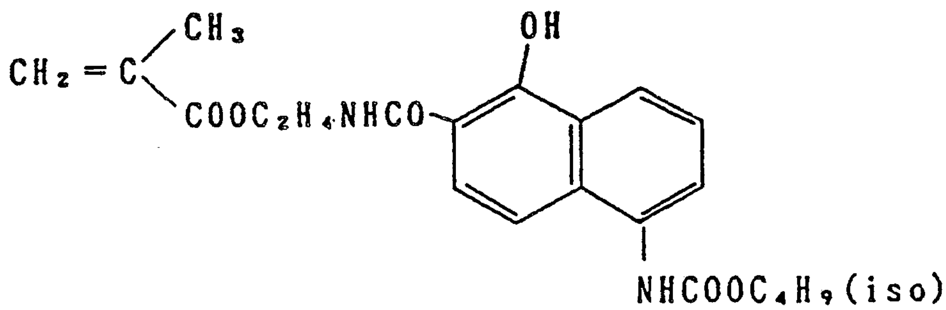
(16)


CH₂=CH
CONH
OH
NHCOC₃F₇

(17)


CH₃
CH₂=C
CONHC₂H₄NHCO
OH

(18)



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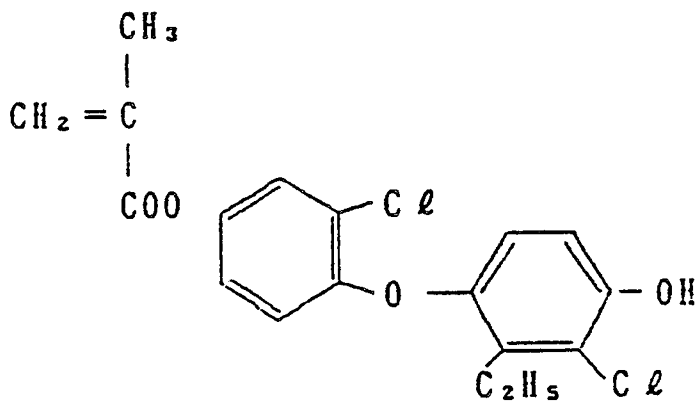
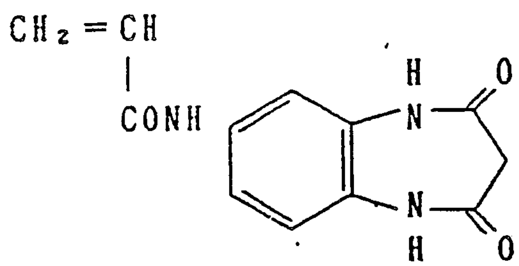


(20)



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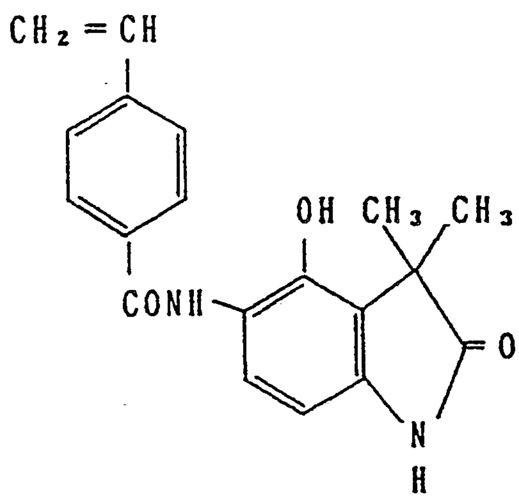
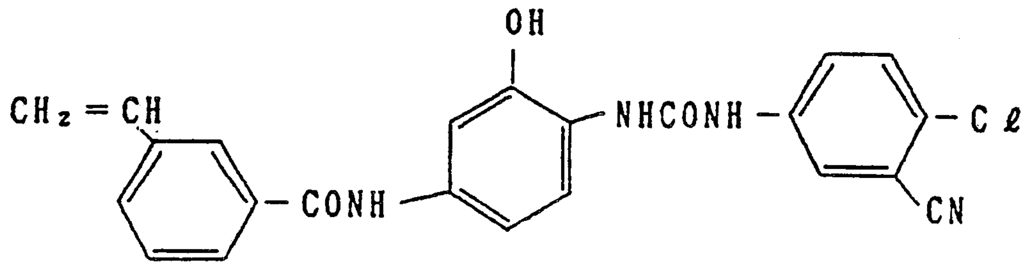
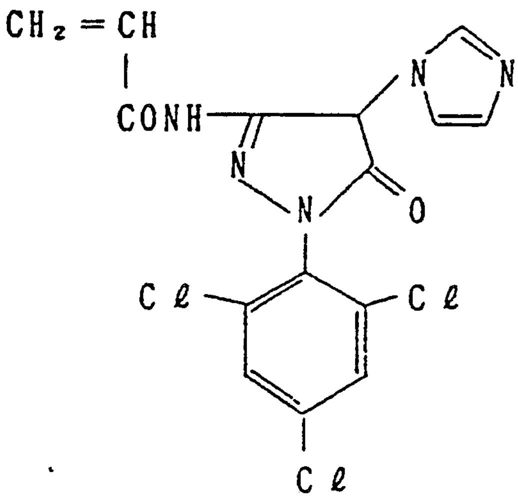


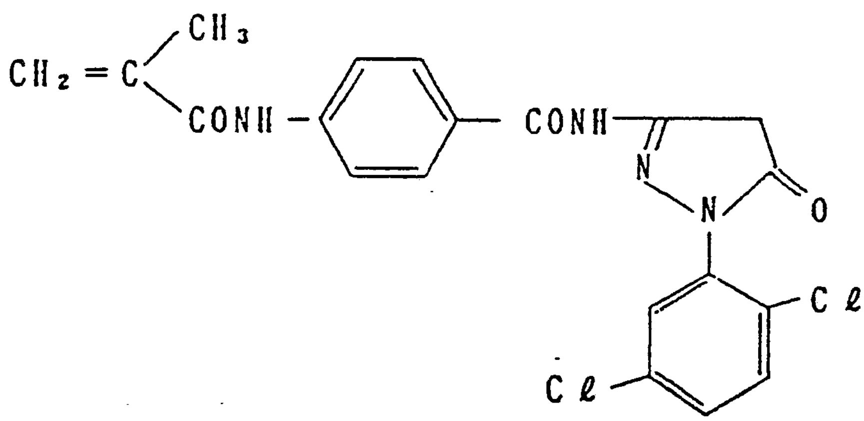
(22)



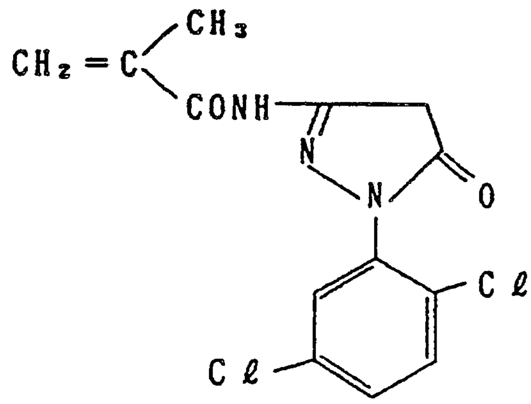
(23)



(24).



(25)



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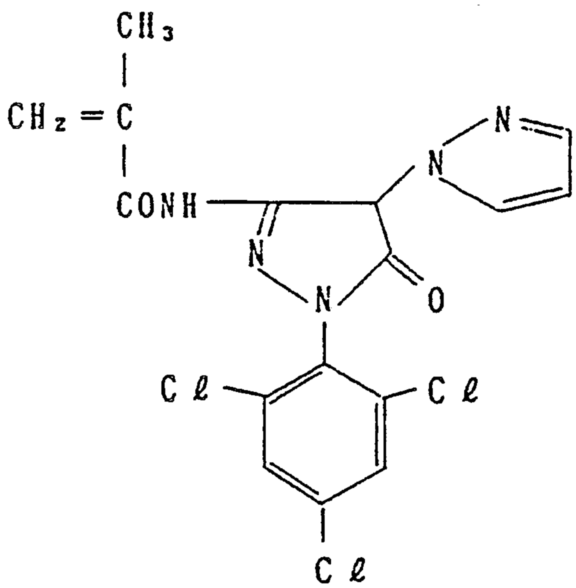
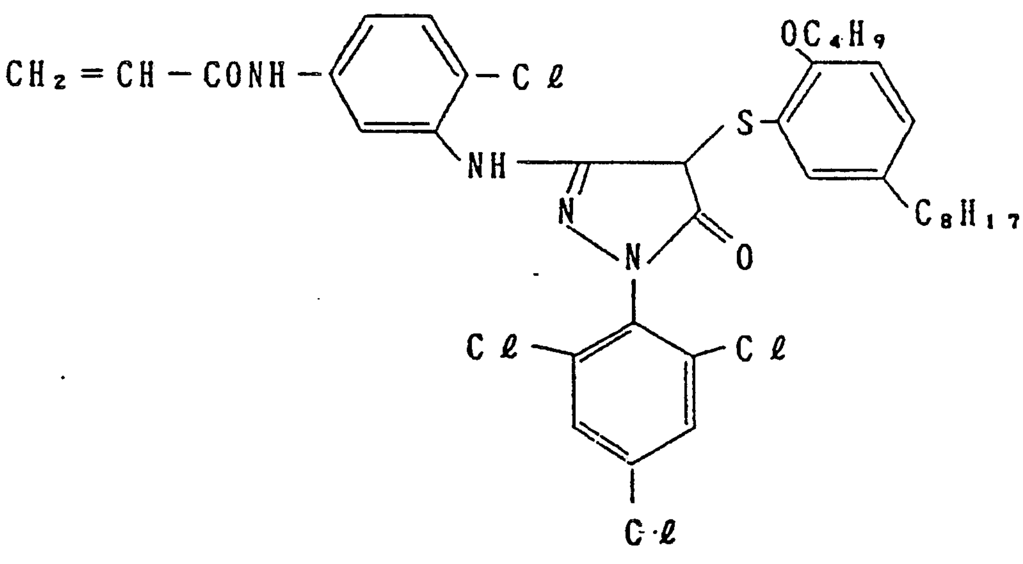
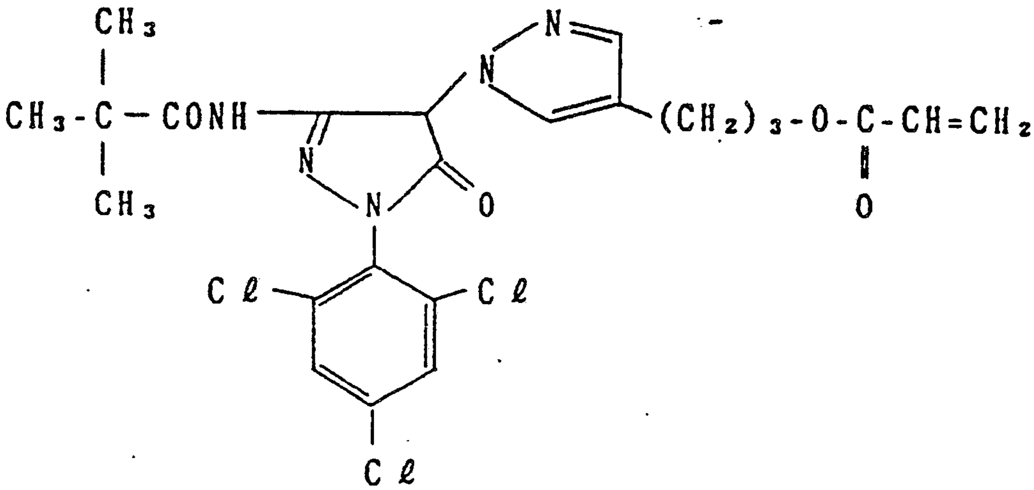


(27)



(28)



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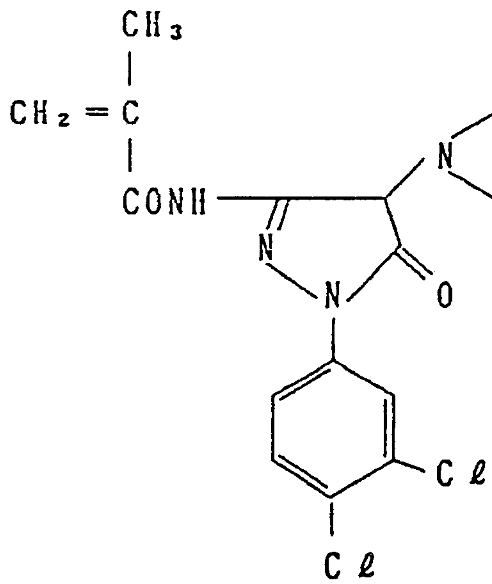
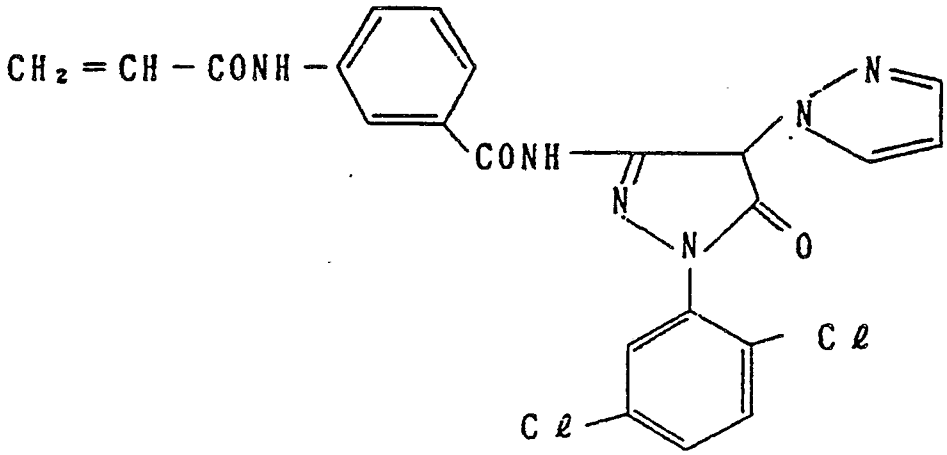
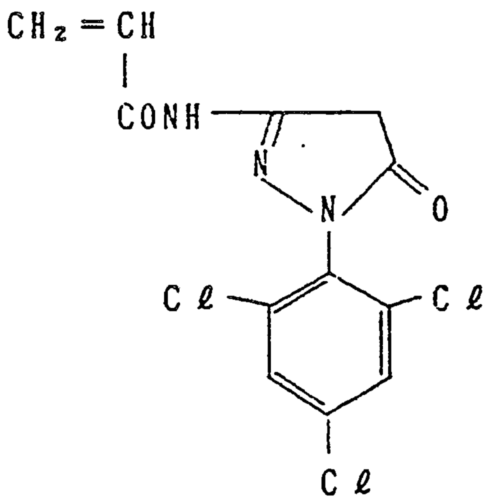


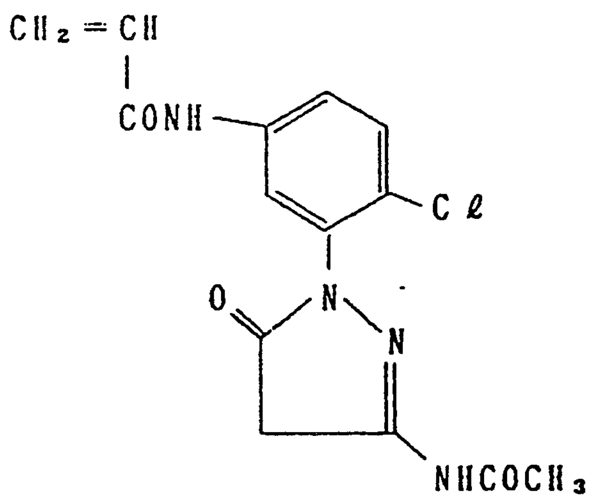
(30)


CH₂=CH−CONH−
CONH
N
N
N
N
O
Cℓ
Cℓ

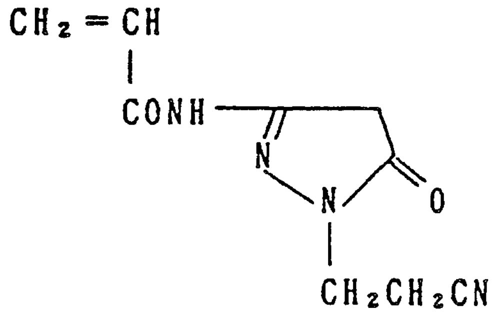
(31)


CH₂=CH
CONH
N
N
O
Cℓ
Cℓ
Cℓ

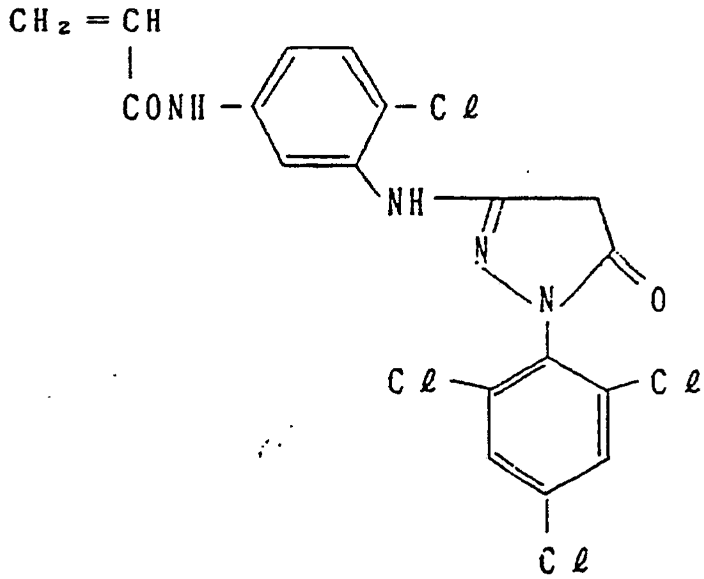
(32)


CH₂=CH
CONH
Cℓ
O
N
N
NHCOCH₃

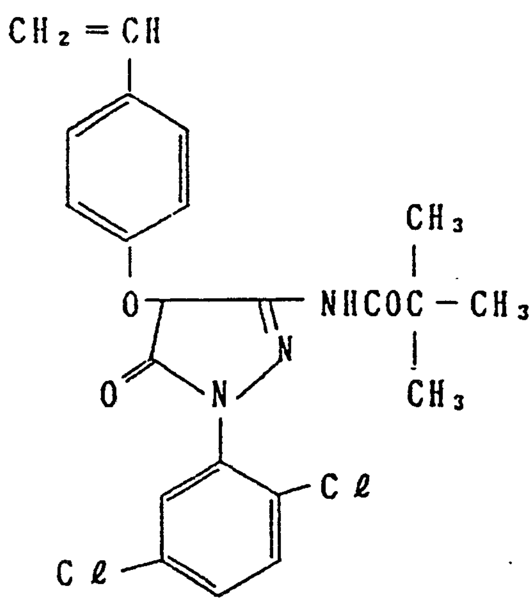
(33)



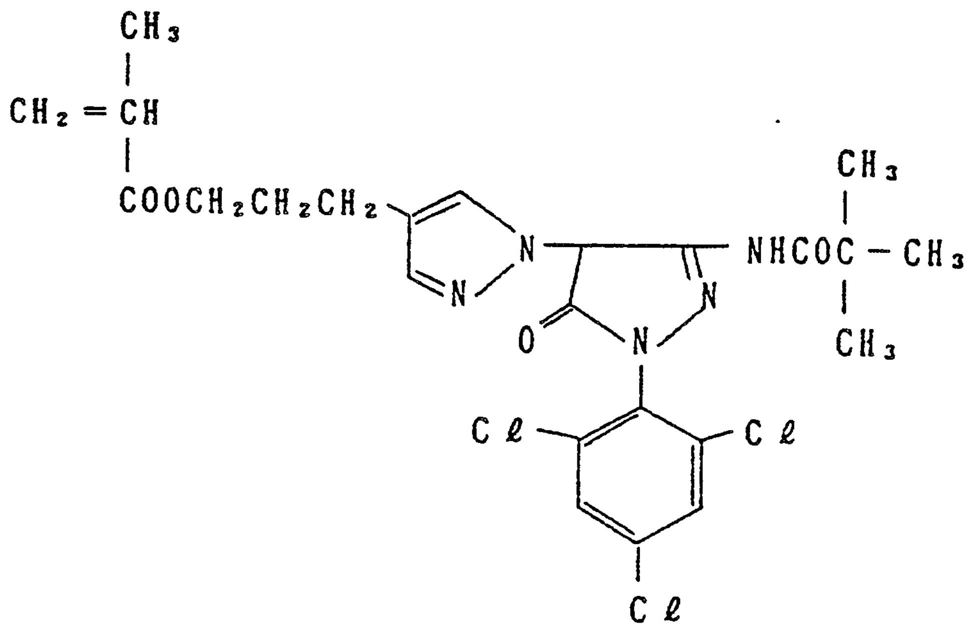
(34)



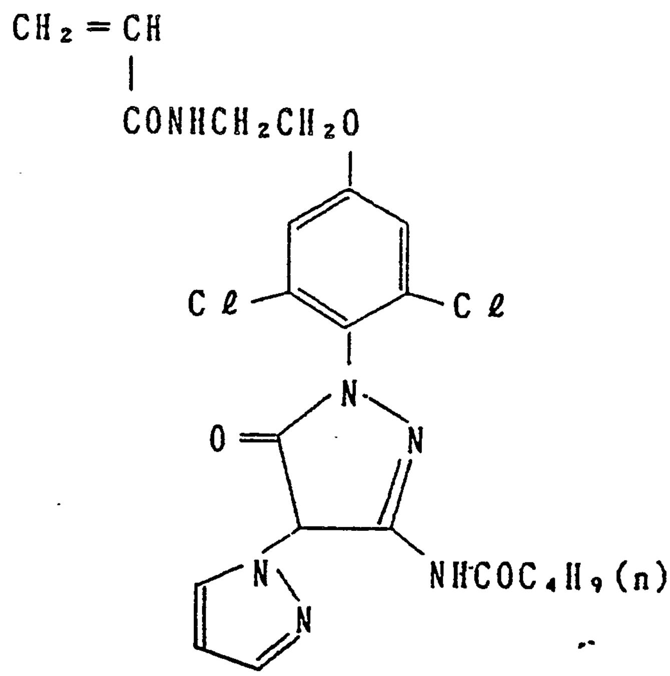
(35)



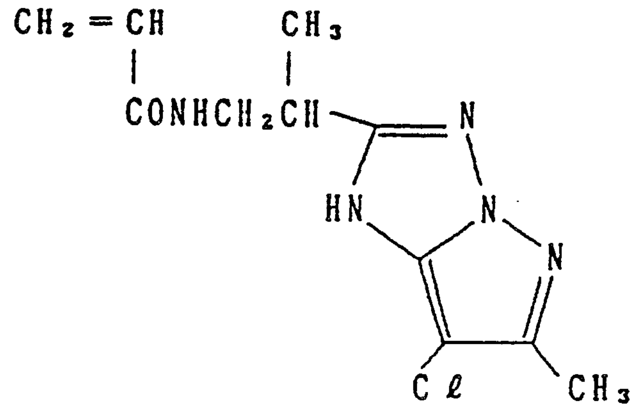
(36)


CH3
CH2 = CH
COOCH2CH2CH2
N
N
CH3
NHCOC - CH3
CH3
N
O
N
Cℓ
Cℓ
Cℓ

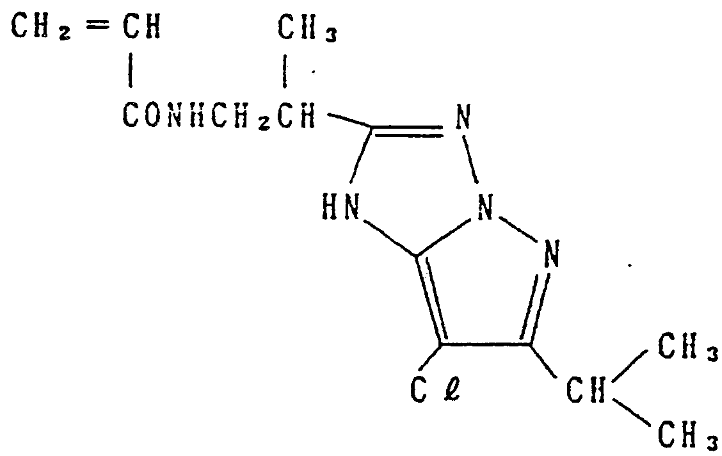
(37)


CH2 = CH
CONHCH2CH2O
Cℓ
Cℓ
N
O
N
N
N
NHCOC4H9(n)

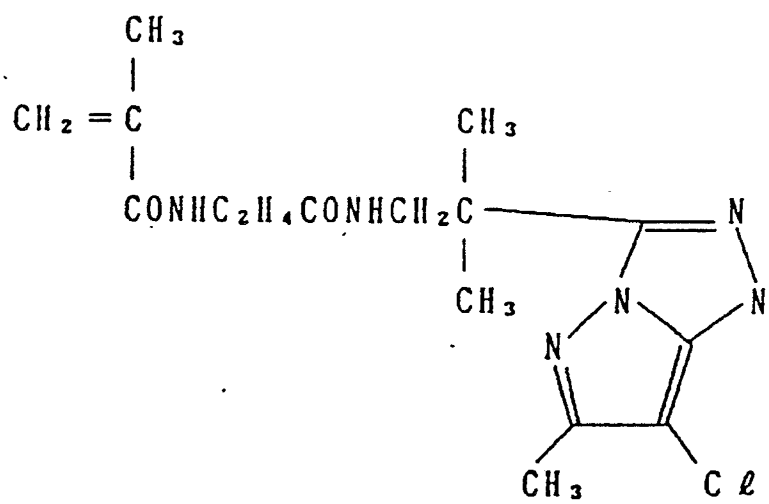
(38)



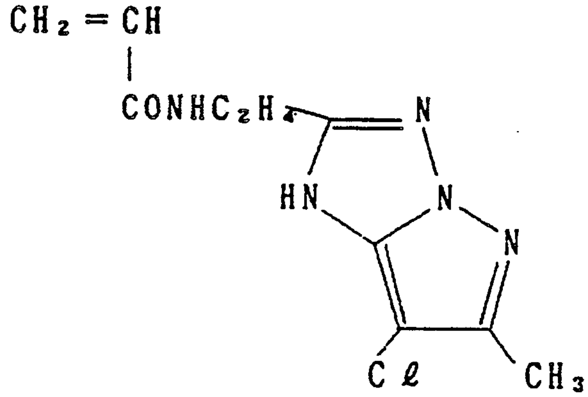
(39)



(40)



(41)



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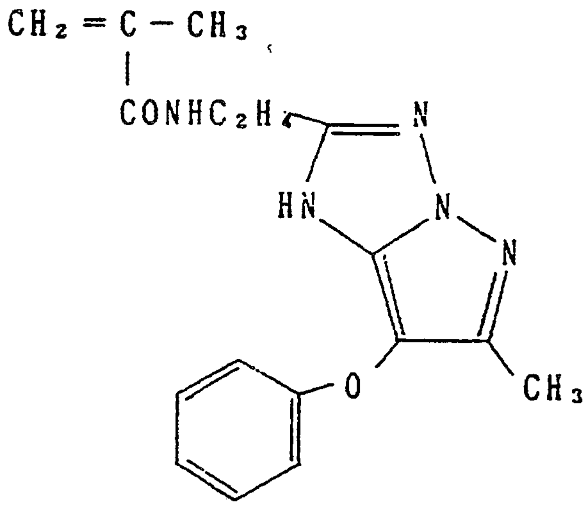

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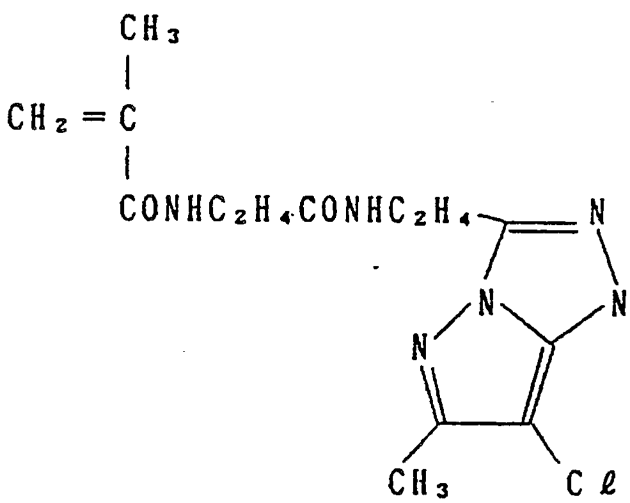

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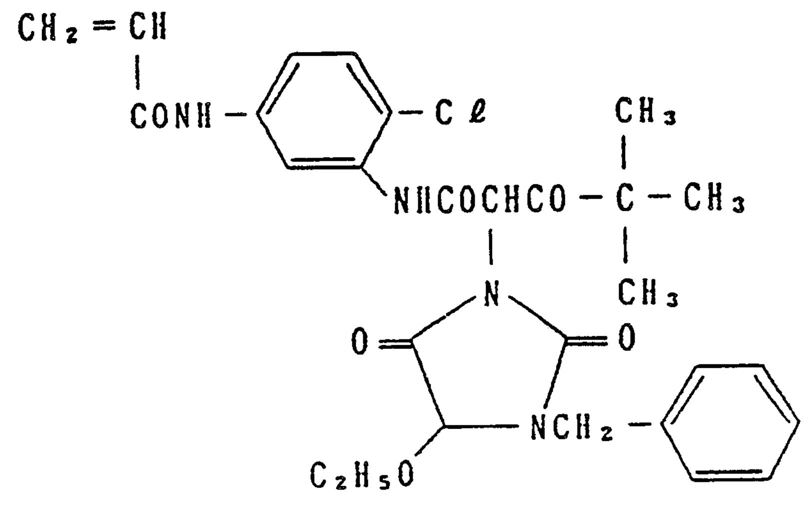

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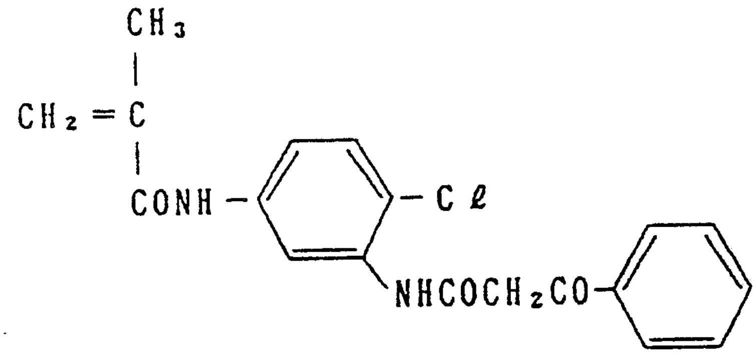

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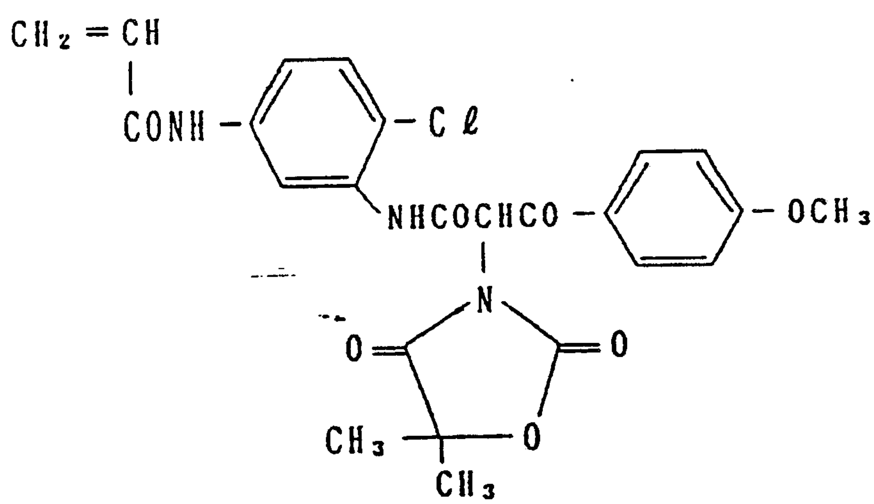

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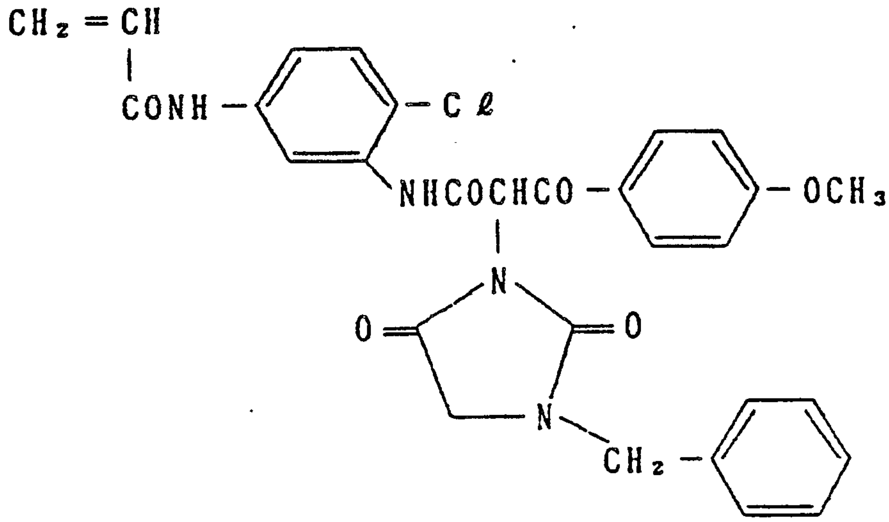

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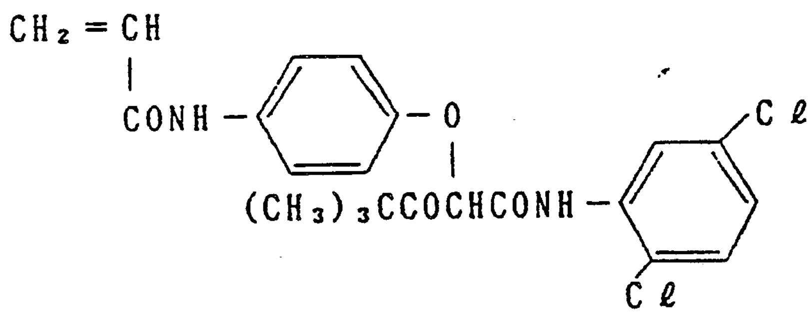

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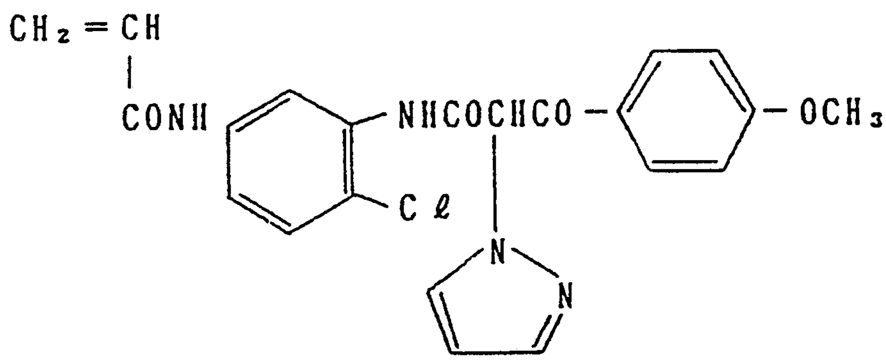

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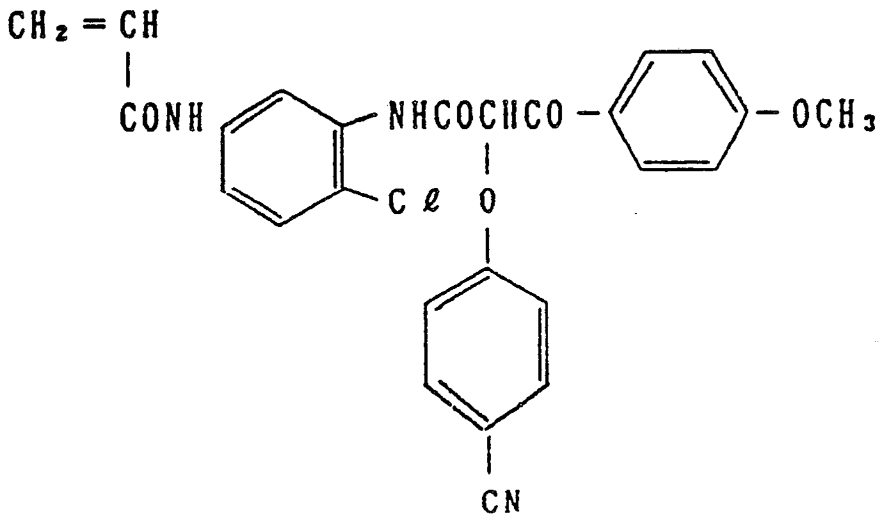

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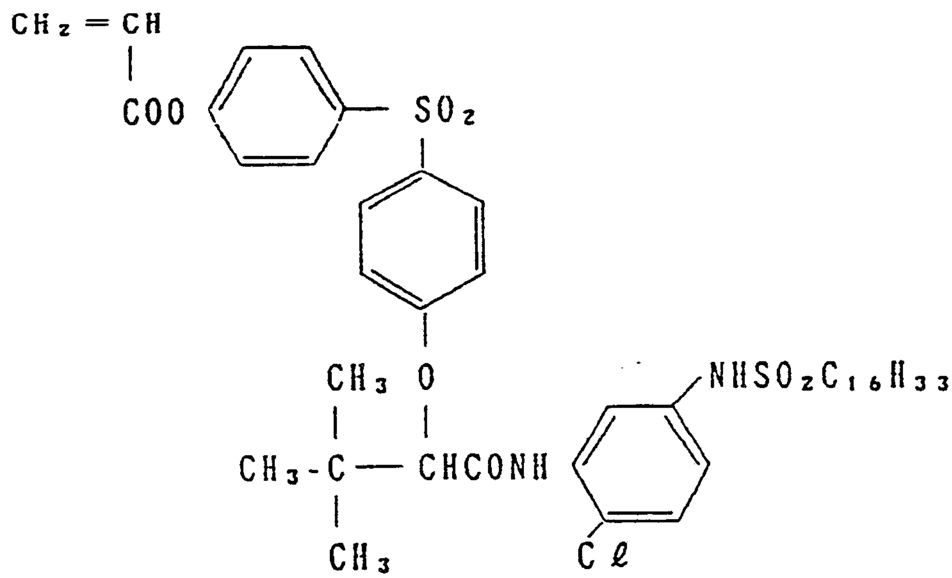

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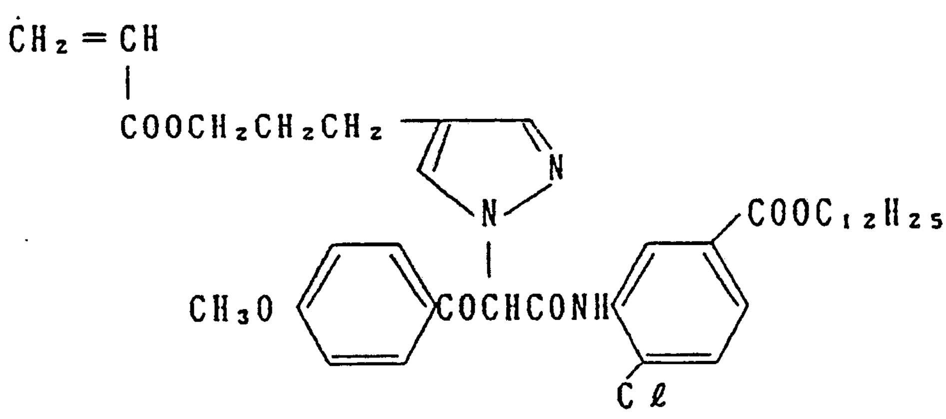
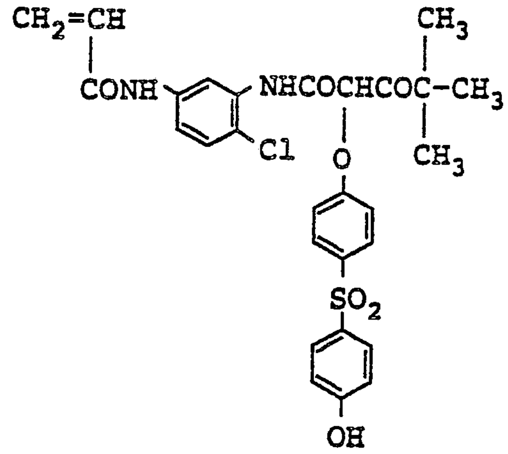


(1)



In the polymeric couplers represented by the general formula [P] and as obtained by means of a polymerization reaction in which the chain transfer agents used in this invention are used about 0.1 to 20 wt% of compounds which can be represented by the general formulae [XXIII] and [XXIV] indicated below, may be present.

General Formula [XXIII]

$E \leftarrow\!(A)_x\!-\!(B)_y\!\rightarrow E$

(Where E, A, B, x and y have the same meaning as before)

General Formula [XXIV]

$I \leftarrow\!(A)_x\!-\!(B)_y\!\rightarrow X$

(Where A, B, x, y and X have the same meaning as before. I represents a group originating from the radical produced by the degradation of the polymerization initiator.)

Furthermore, compounds originating from chain transfer to monomer and chain transfer to solvent are also present in the polymeric couplers, in accordance with the chain transfer potential of the monomer and solvent, as well as the compounds of the general formulae [XXIII] and [XXIV], as described by T. Ohtsu on pages 123 to 127 of "Radical Polymerization (I)" (published by Kagaku Dojin, 1971).

Polymers represented by the general formula [P] which have been prepared using a chain transfer agent in accordance with this invention are known as telomers.

Telomers have been described in detail on pages 10 to 30 of "Oligomers", edited by N. Ohkawara (published by Kodansha Scientific, 1976).

According to this text, the polymerization reaction in a system which contains a chain transfer agent proceeds in the following manner:

Initiation

$I \rightarrow I.$

$I. + EX \rightarrow IX + E.$

$E. + M \rightarrow EM.$

$$\text{Propagation} \quad EM\cdot + (n-1)M \xrightarrow{kp} EMn\cdot$$

$$\text{Chain Transfer} \quad EMn. + EX \xrightarrow{ktr} E\text{-}(Mn)\text{-}X + E\cdot$$

$$\text{Termination} \quad 2\,E\cdot \rightarrow E\text{-}E$$
$$2EMn\cdot \rightarrow E\text{-}(M)_{2n}\text{-}E$$

Here I, M and EX are respectively the initiator, the monomer and the chain transfer agent, EM• are propagating radicals, I•, $E(Mn)_n X$ and E• are respectively the primary radical, the grown polymer and the chain transfer agent radical, and k is the respective rate constant for each elementary reaction.

Thus, polymerization occurs with initiation via a radical which has been transferred to the chain transfer agent, after which reaction proceeds and then chain transfer onto the chain transfer agent occurs.

The chain transfer constant is defined as the ratio of the rate constants of the chain transfer reaction and the propagation reaction, ktr/kp.

Unlike the normal radical polymerization with monomeric polymers, the principal distinguishing feature of the method used to synthesize the telomeric couplers used in this invention is that a chain transfer agent which has at least 8 carbon atoms and which has a chain transfer constant of at least 0.1 but not more than 20 is used.

The use of a chain transfer agent which has at least 8 carbon atoms is necessary in order to render the telomeric coupler fast to diffusion in an emulsion layer, and the use of a chain transfer agent which can be represented by E-X which has a chain transfer constant for the monomeric coupler of at least 0.1 but not more than 20 is effective for minimizing the amount of the compound represented by the general formula [XXIV] which is admixed with the polymeric couplers which are obtained according to this :.nvention.

As described on pages 57 to 102 of the Polymer Handbook II, by J. Bandrup et al., (published by John Wiley and Sons), and on page 128 of "Radical Polymerization (I)" by T. Ohtsu (published by Kagaku Dojin, 1971), the chain transfer constant varies according to the chain transfer agent and the type of monomer involved, and so the amount of chain transfer agent to be added differs according to the molecular weight of the intended telomer and the value of the chain transfer constant.

The chain transfer constant varies with the combination of chain transfer agent and monomeric coupler, but the use of mercaptans as chain transfer agents is preferred since they have a chain transfer constant in the range between 0.1 and 20 irrespective of the type of monomeric coupler.

The preferred chain transfer agents for use in the invention are indicated below, but the chain transfer agent is not limited to those listed here.

$C_8H_{17}SH$, $C_{10}H_{21}SH$, $C_{12}H_{25}SH$,

$C_{14}H_{29}SH$, $C_{15}H_{31}SH$, $C_{16}H_{33}SH$,

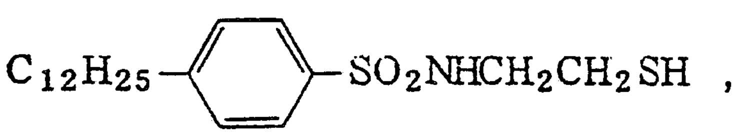
$C_{18}H_{37}SH$, $C_{20}H_{41}SH$, $C_{31}H_{63}SH$,

$C_8H_{17}O\underset{\underset{O}{\|}}{C}CH_2SH$, $C_{12}H_{25}O\underset{\underset{O}{\|}}{C}CH_2SH$,

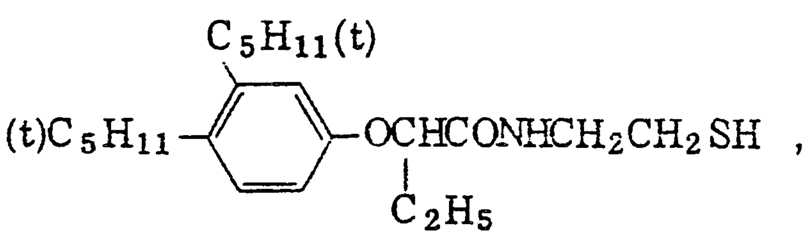
$C_{18}H_{37}O\underset{\underset{O}{\|}}{C}CH_2SH$, $C_2H_5O\underset{\underset{O}{\|}}{C}-\underset{\underset{SH}{|}}{C}HC_{12}H_{25}$,

$C_{12}H_{25}O\underset{\underset{O}{\|}}{C}CH_2CH_2SH$, $C_{18}H_{37}O\underset{\underset{O}{\|}}{C}CH_2CH_2SH$,

$C_{16}H_{33}SO_2NHCH_2CH_2SH$,

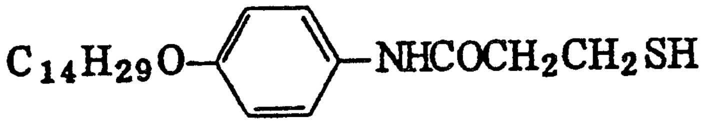


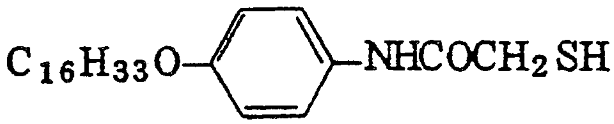
$C_8H_{17}CONHCH_2CH_2SH$, $C_{13},H_{27}CONHCH_2CH_2SH$, $C_{15}H_{31}CONHCH_2CH_2SH$, $C_{17}H_{35}CONHCH_2CH_2SH$,

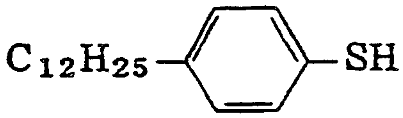
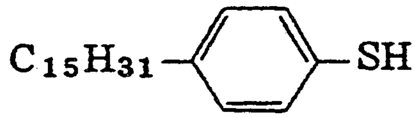


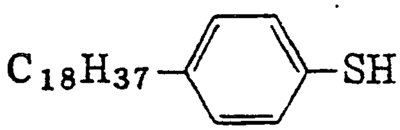
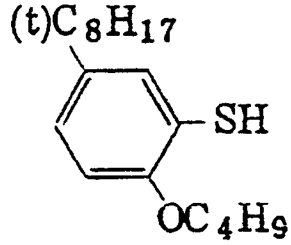
$CH_3CO\overset{\overset{C_{12}H_{25}}{|}}{N}CH_2CH_2SH$, $C_{12}H_{25}NHCH_2CH_2SH$,

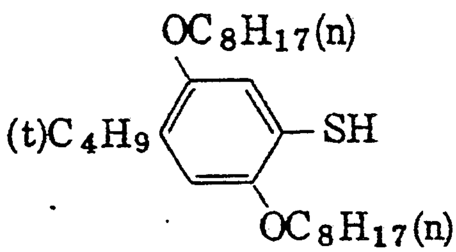
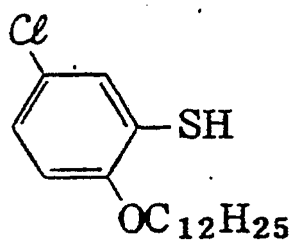
$C_{16}H_{33}NHCH_2CH_2SH$, $C_{12}H_{25}NHCOCH_2SH$, $C_{18}H_{37}NHCOCH_2SH$,

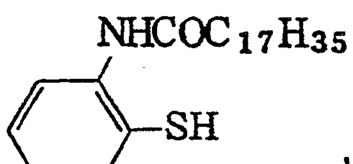
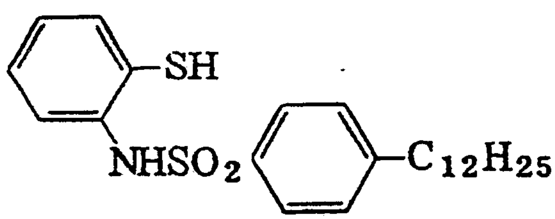
 ,

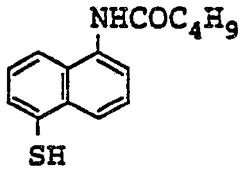
 ,

 ,  ,

 ,  ,

 ,  ,

 ,  ,

 , $BrCH_2COOC_{12}H_{25}$,

$ClCH_2COOC_{12}H_{25}$, $ICH_2COOC_{12}H_{25}$,

$BrCH_2COOC_{16}H_{33}$, $ClCH_2COOC_{18}H_{37}$,

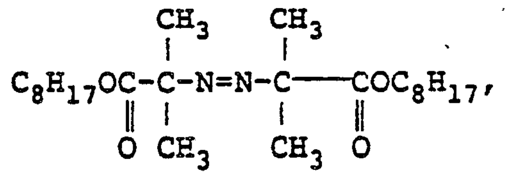
$ICH_2COOC_{18}H_{37}$, $Br_2CHCOOC_{12}H_{25}$,

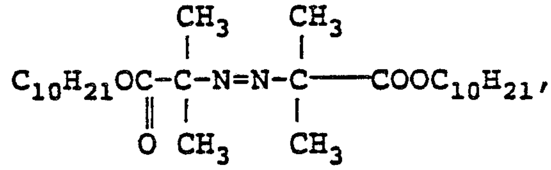
$Cl_3CCOOC_{16}H_{33}$.

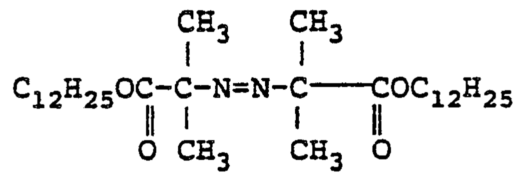
The synthesis of the telomeric couplers of this invention can be achieved using the compounds disclosed in JP-A-56-5543, JP-A-57-94752, JP-A-57-176038, JP-A-57-204038, JP-A-58-28745, JP-A-58-10738, JP-A-58-42044, JP-A-58-145944 and JP-A-59-42543 as polymerization initiators and polymerization solvents.

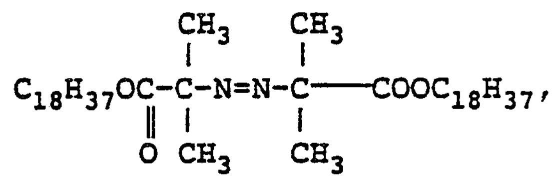
Tlhe use of polymerization initiators which have at least 20 carbon atoms is preferred for the synthesis of the telomeric couplers of this invention. It is possible by using such initiators to increase the fastness to diffusion of the polymeric couplers of the aforementioned general formula [XXIV]

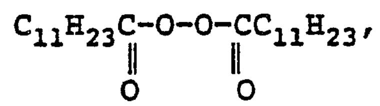
Examples of preferred polymerization initiators are indicated below.

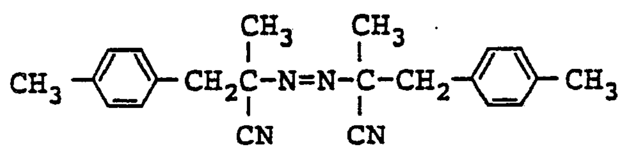












The polymerization initiator is used in an amount of from about 0.01 to about 10 mol%, and preferably in an amount of from 0.01 to 2.0 mol%, with respect to the monomer.

A polymerization solvent which as a low chain transfer constant is best, and those which have a chain transfer constant not exceeding 1×10^{-3} are preferred.

The polymerization temperature must be set in accordance with the molecular weight of the telomer which is being formed and the type of initiating agent which is being used, and although temperatures below 0 °C and above 100 °C can be used, the polymerization is normally carried out at a temperature within the range from 0 °C to 100 °C. Higher temperatures are best for telomer synthesis and the preferred polymerization temperatures are within the range from about 70 °C to 100 °C.

The proportion of the color forming part as represented by the general formula [I] in a telomeric coupler is preferably from 10 to 95 wt% but, in respect of color reproduction, color forming ability and stability, the proportion is preferably from 20 to 90 wt%. In this case the equivalent molecular weight (the number of grams of polymer which contain 1 mol of monomeric coupler) is about 200 to 4,000, but no particular limit is imposed.

Furthermore, the number average molecular weight of a telomeric coupler of this invention is preferably from about 500 to about 10,000, and most desirably from about 500 to about 5,000, from the point of view of color forming ability and speed.

The mercaptan chain transfer agents which are preferably used in the invention are also present in amounts of about 0.01 to 0.3 wt% in the telomeric polymers after completion of the polymerization, and this causes undesirable effects such as fogging and loss of speed etc.

The following methods can be used to eliminate the mercaptans or to render them harmless from the point of view of photographic performance.

(1) The telomeric coupler is precipitated by means of a solvent in which it is essentially insoluble with the recovery of just the telomeric coupler.

(2) Additional fresh ethylenically unsaturated monomer (one which does not contain coupler residual groups) is added after the completion of the polymerization and, on carrying out further polymerization, another telomerization reaction occurs and the mercaptan is deactivated.

(3) The mercaptan is converted by means of an oxidation treatment into a substance (disulfide, sulfone, sulfoxide) which is harmless from the point of view of photographic performance.

The second of these three possible methods is preferred from the point of view of the effectiveness of the reduction in the amount of mercaptan and from the point of view of characteristics such as color forming ability and speed.

Furthermore, by using a monomer which imparts water solubility, such as acrylic acid, or acrylamide, as the ethylenically unsaturated monomer which is added subsequently in method (2) and then carrying out a water re-precipitation process or extraction with a water/organic solvent system after completion of the subsequent polymerization it is possible to eliminate just the mercaptan very efficiently. That is to say, the mercaptans are expelled from the system as water sclubie polymeric telomers of acrylic acid, or acrylamide without affecting the properties of the telomer (which is to say the coupler unit content or color forming performance). Hence, the substances which are harmful in respect of the photographic performance can be removed without affecting the high color forming ability and the high speed properties of the telomer.

It is possible, using this method, to reduce the residual mercaptan content of the telomer to within the range from about 5 ppm to about 100 ppm.

The telomeric couplers of this invention are added to the silver halide emulsion layers or to layers which are adjacent thereto.

The telomeric couplers of this invention are best added at a rate, based on the coupler monomer, of from 0.005 mol to 0.5 mol, and preferably of from 0.01 mol to 0.10 mol, per mol of silver when they are added to the same layer as the silver halide.

Furthermore, the telomeric couplers of this invention when used in non-photosensitive layers, are coated at a rate of from 0.01 to 1.0 gram per square meter, and preferably at a rate of from 0.1 to 0.5 gram per square meter.

The number average molecular weight in this invention can be calculated on the basis of measurements made using gel permeation chromatography (GPC).

The GPC measurement conditions are indicated below. Column: TSKgel (Made by Toyo Soda)
$G1000H_8$
Exclusion Limit Molecular weight 1000 1 column
Column Dimensions 7.51D×600 mm
$G2000H_8$
Exclusion Limit Molecular Weight 10000 2 columns
Column Dimensions 7.51D×600 mm
TSKgel (Made by Toyo Soda)
$G4000H_8$
Exclusion Limit Molecular Weight 400000 1 column
Column Dimensions 7.51D×600 mm Solvent: THF
Flow Rate: 1 ml/min.
Column Temperature: 40 °C
Detector: UV-8 model II
(made by Toyo Soda

A calibration curve was prepared using TSK Standard Polystyrene (made by Toyo Soda).

The number average molecular weight was obtained using the method described on pages 204 to 208 of the Polymer Society publication entitled "Experimental Methods in Polymer Science" (published by Tokyo Kagaku Dojin, 1981), which is to say that it was calculated using a segment method. Thus, the chromatogram obtained was divided into equally spaced counts (D), the peak height from the base line for the ith molecular weight fraction was taken as Hi and the number average molecular weight was obtained using the relationship shown in equation (1) below.

$$\text{Mn (Number average molecular weight)} = \frac{\Sigma MiNi}{\Sigma iNi}$$

$$= \frac{\Sigma iHiD}{\Sigma i(HiD/Mi)}$$

$$= \frac{\Sigma iHi}{\Sigma i(Hi/Mi)}$$

Hence:

$$Mn = \frac{1}{\Sigma(1/Mi)(H\Sigma/\Sigma jHj)} \quad (1)$$

Hence, Ni represents the number of molecules of the ith type, and Mi represents the molecular weight of the molecules of the ith type (Mi can be obtained from the aforementioned claibration curve).

The chain transfer constant in this invention can be calculated in various ways. The method described on pages 126 to 127 of "Radical Polymerization (I)" by T. Ohtsu (published by Kagaku Dojin, 1971) can be used as a general method. Thus, the residual monomeric coupler and the residual chain transfer agent in the reaction mixture in a polymerization reaction where x and y in general formula [P] are 100 and 0 respectively are determined and the chain transfer constant is obtained using equation (2) as shown below.

$$\text{Cs (Chain Transfer Constant)} = \frac{d(\log[S])}{d(\log[M])} \quad (2)$$

Here [S] represents the concentration of residual chain transfer agent and M represents the concentration of residual monomeric coupler.

As is well known in the field of polymeric color couplers, selection of the monomer represented by the general formula [I] can be made in such a way as to have a good affect on the physical and/or chemical properties, which is to say the solubility, compatibility with the binders such as gelation which are used in photographic colloid compositions, flexibility, or thermal stability, of the copolymer.

The telomeric couplers of this invention may be prepared in the form of a latex by dissolving the coupler obtained by polymerization of the monomeric coupler in an organic solvent and emulsifying and dispersing this in an aqueous gelatin solution, or by using a direct emulsion polymerization method.

The methods of emulsification and dispersion of the coupler in the form of a latex in an aqueous gelatin solution disclosed in U.S. Patent 3,451,820 and the methods of emulsion polymerization disclosed in U.S. Patents 4,080,211 and 3,370,952 can be used for this purpose.

Typical examples of the Synthesis of telomeric couplers of this invention are described below.

Examples of Synthesis 1

Telomeric Coupler I (A Copolymer of Monomeric Coupler (1) and Butyl Acrylate)

Fifteen grams of 5-acrylamido-2,4-dichloro-3-methylphenol (monomeric coupler (1)), 12 grams of butyl acrylate, 2.5 grams of n-dodecylmercaptan and 200 ml of N,N-dimethylacetamide were placed in a three necked flask of 300 ml capacity and the mixture was heated to 75°C and stirred under a blanket of nitrogen. Next, 10 ml of an N,N-dimethylacetamide solution which contained 0.3 gram of dimethyl azobisbutyrate was added and polymerization was initiated. After reacting for a period of 5 hours the reaction mixture was cooled to 70°C. Eight grams of acrylic acid and 5 ml of an N,N-dimethylacetamide solution which contained 0.1 gram of dimethyl azobisisobutyrate was added and the mixture was heated and stirred for a further period of 4 hours.

After reaction, the cooled reaction mixture was poured into 3 liters of water and the solid which precipitated out was recovered by filtration and washed thoroughly with water.

It was confirmed by chlorine analysis that this telomeric coupler contained 49.8 wt% of the monomeric coupler (1) units. The number average molecular weight by GPC was 2,800.

The chain transfer constant of the dodecylmercaptan used in this reaction was calculated on the basis of measurements made using gas chromatography and the GPC method indicated below.

Fifteen grams of monomeric coupler (1), 2.5 grams of n-dodecylmercaptan and 200 ml of N,N-dimethylacetamide were placed in a three necked flask of 300 ml capacity and the mixture was heated to 75 °C and stirred under a blanket of nitrogen. Next, 10 ml of an N,N-dimethylacetamide solution which contained 0.3 grams of dimethylazobisisobutyrate was added and polymerization was initiated. Ten ml samples of the reaction mixture were extracted at prescribed intervals, 1 ml of a methanol solution which contained 10 mg of hydroquinone was added to each sample and the polymerization was stopped. The residual amounts of coupler and chain transfer agent in these samples were estimated using the GPC method and gas chromatography respectively, a plot was made of log[monomeric coupler] and log[chain transfer agent] and a chain transfer constant of 3.5 was obtained using the aforementioned equation (2).

The telomeric couplers (II) to (XX) shown in table 1 were prepared in the same way as described in example of synthesis 1 (these reactions were carried out with adjustment of the amount of chain transfer agent in order to adjust the moledular weight).

Table 1

Example of Synthesis	Telomeric Coupler	Monomeric Coupler Type	Monomeric Coupler Wt (g)	Non-Color forming Monomer Type*2	Non-Color forming Monomer Wt (g)	Chain Transfer Agent	Chain Transfer Constant*1	Monomeric Coupler Unit content of Polymer (wt%)	Number Average Molecular Weight
1	I	(1)	15	BA	12	$C_{12}H_{25}SH$	3.5	51.3	2800
2	II	(1)	15	EA	4	$C_{12}H_{25}SH$	3.5	74.2	1900
3	III	(2)	12	BA	10	$C_{12}H_{25}SH$	2.6	50.8	2100
4	IV	(14)	15	BA	11	$C_{12}H_{25}SH$	2.9	49.8	2800
5	V	(14)	12	MEA	10	*3	1.1	50.7	2300
6	VI	(14)	15	BA	3	$C_{18}H_{37}SH$	2.3	73.8	1700
7	VII	(14)	15	-		$C_{12}H_{25}SH$	2.9	89.5	2000
8	VIII	(23)	30	BA	25	$C_{12}H_{25}SH$	3.0	50.5	1700
9	IX	(25)	15	St	4	$C_{12}H_{25}SH$	1.8	75.9	3000
10	X	(26)	12	BA	9	$C_{12}H_{25}SH$	3.2	55.5	2500
11	XII	(26)	12	BA	10	$C_{18}H_{37}SH$	1.8	50.3	1700
12	XII	(26)	15	BA	5	$C_{12}H_{25}SH$	3.2	70.5	3000
13	XIII	(26)	15	-		$C_{12}H_{25}SH$	3.2	90.4	1500

Table 1 (cont'd)

Example of Synthesis	Telomeric Coupler	Monomeric Coupler Type	Monomeric Coupler Wt (g)	Non-Color forming Monomer Type*2	Non-Color forming Monomer Wt (g)	Chain Transfer Agent	Chain Transfer Constant*1	Monomeric Coupler Unit content of Polymer (wt%)	Number Average Molecular Weight
14	XIV	(27)	15	BA	12	$C_{12}H_{25}SH$	2.8	48.6	3200
15	XV	(27)	15	MEA	4	$C_{12}H_{25}SH$	2.8	72.2	1900
16	XVI	(41)	15	BA	12	$C_{12}H_{25}SH$	3.7	48.7	2600
17	XVII	(42)	12	BA	10	$C_{18}H_{37}SH$	2.5	50.7	3000
18	XVIII	(47)	20	-		$C_{18}H_{37}SH$	4.2	84.0	3200
19	XIX	(49)	20	MA	12	$C_{12}H_{25}SH$	0.36	58.0	3900
20	XX	(49)	15	MMA	3	$C_{12}H_{25}SH$	0.36	73.2	2800

*1 Chain transfer constant of the chain transfer agent for the coupler monomer.

*2: MA - Methyl Acrylate, EA - Ethyl Acrylate, BA - Butyl Acrylate, MMA - Methyl Methacrylate, MEA - 2-Methoxyethyl Acrylate

*3: $C_2H_5CH(CH_3)-(CH_2)_4-OC(=O)CH_2SH$

Comparative Example of Synthesis 1

(Copolymer of the Monomeric Coupler (14) and Butyl Acrylate)

A mixture consisting of 20 grams of monomeric coupler (14), 20 grams of butyl acrylate and 200 ml of ethyl acetate was heated to 75 °C while being stirred under a blanket of nitrogen, and then 10 ml of an ethyl acetate solution which contained 0.5 grams of dimethyl azobisisobutyrate was added and polymerization was initiated. The reaction mixture was cooled after reacting for a period of 5 hours and then concentrated without further treatment.

The solid which precipitated out was dried by heating under reduced pressure and 37.3 grams of the comparative polymeric copolymer (A) was obtained.

It was confirmed by fluorine analysis that this polymeric coupler had a monomeric coupler (14} unit content of 50.2 wt%. The number average molecular weight by GPC was 41,000.

Comparative Example of Synthesis 2

(Copolymer of Monomeric Coupler (14) and Butyl Acrylate)

Comparative polymeric coupler (B) was synthesized in using 30 grams of monomeric coupler (14) and 10 grams of butyl acrylate by following the same procedure as in comparative example of synthesis 1. The monomeric coupler (14) unit content was found, by fluorine analysis, to be 74.6 wt%, and the number average molecular weight by GPC was 18,000.

Comparative Example of Synthesis 3

(Copolymer of Monomeric Coupler (14) and Butyl Acrylate)

Comparative polymeric coupler (C) was obtained under the same conditions as in comparative example of synthesis 1 except that ten times the amount of polymerization solvent and four times the amount of polymerization initiator were used.

Comparative Polymeric Coupler (C)

Number average molecular weight 3,700
Coupler unit content in polymer 48.7 wt%

Comparative Example of Synthesis 4

Copolymer of Monomeric Coupler (14) and Butyl Acrylate)

Comparative polymeric coupler (D) was obtained under the same conditions as in comparative example of synthesis 2 except that eight times the amount of polymerization solvent and two times the amount of polymerization initiator were used.

Comparative Polymeric Coupler (D)

Number average molecular weight 3,200
Coupler unit content in polymer 73.9 wt%

Comparative Example of Synthesis 5

(Copolymer of 1-(2,4,6-Trichlorophenyl)-3 methacrylamido-4-pyrazolyl-2-pyrazolin-5-one (Monomeric Coupler (26) and Butyl Acrylate)

A mixture consisting of 20 grams of monomeric coupler (26), 20 grams of butyl acrylate and 150 grams of dimethylacetamide was heated to 75 °C with stirring under a blanket of nitrogen and then 10 ml of a dimethylacetamide solution which contained 1.0 gram of dimethyl azobisisobutyrate was added and polymerization was initiated. The reaction mixture was cooled after reacting for a period of 5 hours and then poured into 3 liters of water, and the solid which precipitated out was recovered by filtration and washed thoroughly with water. The solid was dried by heating under reduced pressure and 38.5 grams of comparative polymeric coupler (E) was obtained.

It was confirmed, by chlorine analysis, that this polymeric coupler had a monomeric coupler (26) unit content of 50.8 wt%. The number average molecular weight by GPC was 210,000.

Comparative Example of Synthesis 6

(Copolymer of Monomeric Coupler (26) and Butyl Acrylate)

Comparative polymeric coupler (F) was synthesized in using 30 grams of monomeric coupler (26) and 10 grams of butyl acrylate by following the same procedure as in comparative example of synthesis 3. The monomeric coupler (14) unit content was found, by fluorine analysis (sic), to be 75.3 wt%, and the number average molecular weight by GPC was 3,000.

Comparative Example of Synthesis 7

(Copolymer of Monomeric Coupler (26) and Butyl Acrylate)

Comparative polymeric coupler (G) was obtained under the same conditions as in comparative example of synthesis 5 except that four times the amount of polymerization solvent and ten times the amount of polymerization initiator were used.

Comparative Polymeric Coupler (G)

Number average molecular weight 3,600
Coupler unit content in polymer 48.5 wt%

Comparative Example of Synthesis 8

(Copolymer of Monomeric Coupler (26) and Butyl Acrylate)

Comparative polymeric coupler (H) was obtained under the same conditions as in comparative example of synthesis 6 except that four times the amount of polymerization solvent and three times the amount of polymerization initiator were used.

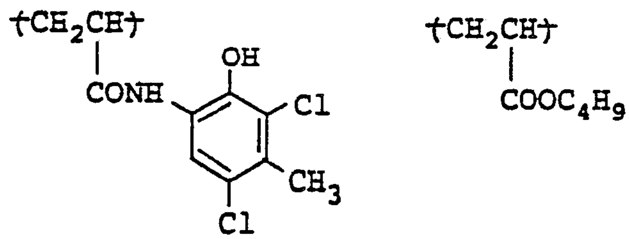
Comparative Polymeric Coupler (H)

Number average molecular weight 3,800
Coupler unit content in polymer 73.6 wt%

Comparative Examples of Synthesis 9 to 12

(Copolymers of Monomerci Coupler (1) and Butyl Acrylate)

Comparative polymeric couplers (I) to (L) were synthesized under the same conditions as used in comparative examples 1 to 4 respectively.



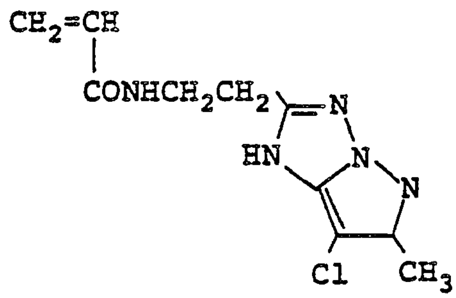
Comparative Ex. of Synthesis	Compound	Coupler Monomer Content (wt%)	Number Ave. Mol. Wt.
9	(I)	51.9	44,000
10	(J)	50.8	3,700
11	(K)	74.9	15,600
12	(L)	75.7	3,500

Comparative Examples of Synthesis 13 to 16

(Copolymers of Monomeric Coupler (41) (examples 13 and 14) or Monomeric Coupler (27) (examples 15 and 16) and Butyl Acrylate)

Monomeric Couplers

(41)



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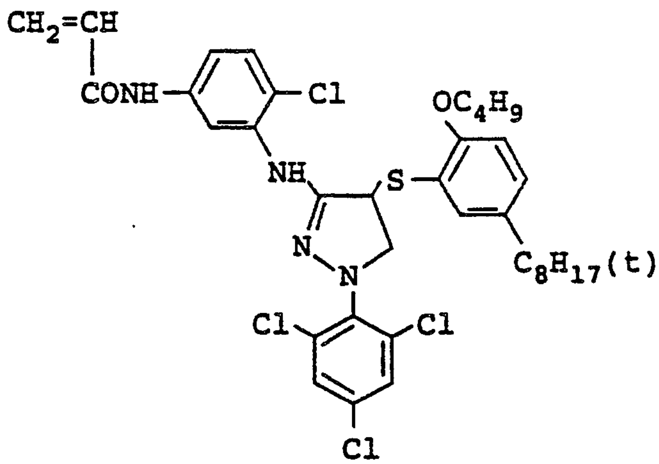


The comparative polymeric couplers (M) and (O) were synthesized under the same conditions as in comparative example of synthesis 5 and the comparative polymeric couplers (N) and (P) were synthesized under the same conditions as in comparative example of synthesis 6.

Comparative Example of Synthesis	13	14	15	16
Compound	(M)	(N)	(O)	(P)
Monomeric Coupler	(41)	(41)	(27)	(27)
Non-color Forming Monomer	BA	BA	BA	BA
Coupler Unit Content (wt%)	50.0	50.8	46.4	50.8
Number Average Mol. Wt. (x100)	360	35	230	25

Comparative Example of Synthesis 17

(Copolymer of Monomeric Coupler (14) and Butyl Acrylate)

A mixture consisting of 12 grams of monomeric coupler (14), 10 grams of butyl acrylate, 3.0 grams of

2-hexadecanol (chain transfer constant 1×10^{-3}) and 20 ml of methanol was heated to 75 °C with stirring under a blanket of nitrogen and then 10 ml of an ethanol solution which contained 0.5 gram of dimethyl azobisisobutyrate was added and polymerization was initiated. The reaction mixture was cooled after reacting for a period of 5 hours and then poured into 1.5 liters of water, and the solid which precipitated out was recovered by filtration and washed thoroughly with water.

The solid was dried by heating under reduced pressure and 20.8 grams of comparative polymeric coupler (Q) was obtained.

It was confirmed by fluorine analysis that this polymeric coupler had a monomeric coupler (14) unit content of 49.5 wt%. The number average molecular weight by GPC was 290,000.

Comparative Example of Synthesis 18

(Copolymer of 1-(2,4,6-trichlorophenyl)-3-methacrylamido-4-pyrazol-2-pyrazolin-5-one (Monomeric Coupler (26)) and Butyl Acrylate)

A mixture consisting of 20 grams of monomeric coupler (26), 17 grams of butyl acrylate, 3.0 grams of 2-hexadecanol and 150 grams of dimethylacetamide was heated to 75 °C with stirring under a blanket of nitrogen and then 10 ml of a dimethylacetamide solution which contained 1.0 gram of dimethyl azobisisobutyrate was added and polymerization was initiated. The reaction mixture was cooled after reacting for a period of 5 hours and then poured into 3 liters of water, and the solid which precipitated out was recovered by filtration and washed thoroughly with water. This solid was dried by heating under reduced pressure and 36.8 grams of comparative polymeric coupler (R) was obtained.

It was confirmed by chlorine analysis that this polymeric coupler had monomeric coupler (26) unit content of 51.4 wt%. The number average molecular weight by GPC was 15,000.

Comparative Example of Synthesis 19

(Copolymeric of Monomeric Coupler (1) and Butyl Acrylate)

Comparative polymeric coupler (S) (37.2 grams) was Synthesized under the same conditions as in comparative example of synthesis 17 using 20 grams of monomeric coupler (1), 17 grams of butyl acrylate and 3.0 grams of 2-hexadecanol.

According to the results of chlorine analysis, this compound contained 49.7% of monomeric couDler. (1) units and the number average molecular weight by GPC was 29,000.

Comparative Example of Synthesis 20

(Copolymer of Monomeric Coupler (27) and Butyl Acrylate)

Comparative polymeric coupler (T) (35.2 grams) was synthesized under the same conditions as in comparative example of synthesis 18 using 20 grams of monomeric coupler (27), 17 grams of butyl acrylate and 3.0 grams of 2-hexadecanol.

According to the results of chlorine analysis, this compound contained 50.9% of monomeric coupler (27) units, and the number average molecular weight by GPC was 20,000.

The silver halide which is contained in the photographic emulsion layer of a photographic material to which the invention is being applied is preferably a silver iodobromide, silver iodochloride or silver iodochlorobromide which contains not more than about 30 mol% of silver iodide. The use of silver iodobromides which contain from about 2 mol% to about 25 mol% of silver iodide is most desirable.

The silver halide grains in the photographic emulsion may have a regular crystalline form, such as a cubic, octahedral or tetradecahedral form, an irregular crystalline form, such as a spherical or tabular form, they may have crystal defects such as twinned crystal planes, or they may have a composite form consisting of these forms.

The silver halide grains may be of a small size nQt more than about 0.2 microns, or of a large size such that the projected area diameter is up to about 10 microns, and they may take the form of a polydispersion or a mono-dispersion.

The silver halide photographic emulsions which can be used in the invention can be prepared, for example, using the methods disclosed for example in Research Disclosure (RD) No. 17643 (December 1978), pages 22 to 23, "I. Emulsion Preparation and Types", and in RD No. 18716 (November 1979), page 648; in Chemie et Phvsioue Photographique, by P. Glafkides, published by Paul Montel, 1967; in Photographic Emulsion Chemistry, by G.F. Duffin, published by Focal Press, 1966; and in . Making and Coating Photographic Emulsions, by V.L. Zelikman et al., published by Focal Press, 1964, etc.

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

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

The crystal structure may be uniform, the interior and exterior parts may have a heterogeneous halogen composition, or the grains may have a layered structure and, moreover, the silver halides which have different compositions may be joined with an epitaxial junction or they may be joined with compounds other than silver halides such as silver thiocyanate or lead oxide etc.

Mixtures of grains of various crystalline forms may also be used.

The silver halide emulsions used have normally been subjected to physical ripening, chemical ripening and spectral sensitization. Additives which can be used in these processes have been disclosed in Research Disclosure Nos. 17643 and 18716, and the locations of the said disclosures are summarized in the table below.

Known photographically useful additives which can be used in the invention are also disclosed in the two Research Disclosures mentioned above, and the locations of these disclosures are also shown in the table below.

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

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

The couplers disclosed in U.S. Patents 3,933,501, 4,022,620, 4,326,024 and 4,401,752, in JP-B-58-10739 (the term "JP-B" as used herein means an "examined Japanese patent publication"), and in British Patents 1,425,020 and 1,476,760 are preferred as yellow couplers.

The 5-pyrazolone based, and pyrazoloazole based, compounds are preferred as magenta couplers, and those disclosed in U.S. Patents 4,310,619 and 4,351,897, in EP-B-73,636, in U.S. Patents 3,061,432 and 3,725,067, in Research Disclosure No. 24220 (June 1984), in JP-A-60-33552, in Research Disclosure No. 24230 (June 1984), in JP-A-60-43659, and in U.S. Patents 4,500,630 and 4,540,654 are most desirable.

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

The colored couplers for correcting the unwanted absorptions of the colored dyes disclosed in Research Disclosure No. 17643 section VII-G, in U.S. Patent 4,163,670, in JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, and in British Patent 1,146,368 are preferred.

The couplers of which the colored dyes have a suitable degree of diffusibility disclosed in U.S. Patent 4,366,237, in British Patent 2,125,570, in EP-B-96,570, and in West German Patent (Laid-open) No. 3,234,533 are preferred.

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

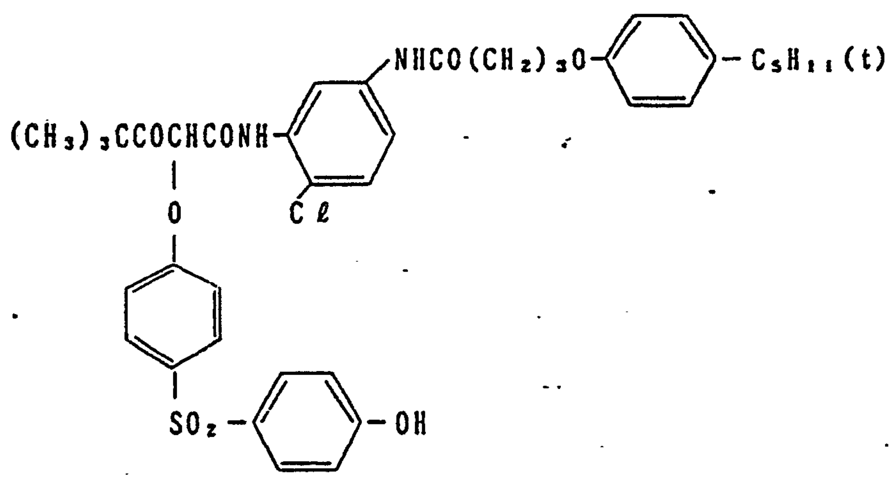
Couplers which release photographically useful residual groups on coupling can also be used preferentially in this invention. The DIR couplers which release development inhibitors desclosed in the patents disclosed in the aforementioned Research Disclosure No. 17643, section VII-F, in JP-A-57-151944, 57 154234 and 60-184248, and in U.S. Patent 4,248,962 are preferred.

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

Other couplers which can be used in the light sensitive materials of this invention include the competitive couplers disclosed in U.S. Patent 4,130,427 etc., the multi-equivalent couplers disclosed in U.S. Patents 4,283,472, 4,338,393 and 4,310,618, the DIR and redox compound releasing couplers disclosed in JP-A-60-185950 and 62-24252, the couplers which release a dye to which color is restored after elimination as disclosed in EP-A-173,302, the bleaching accelerator releasing couplers disclosed in Research Disclosure Nos. 11449 and 24241, and in JP-A-61-201247, and the ligand releasing couplers disclosed in U.S. Patent 4,553,477.

Actual examples of color couplers which can be used in the invention in addition to the polymeric couplers described above are indicated below, but the invention is not limited to these color couplers.

C-(1)



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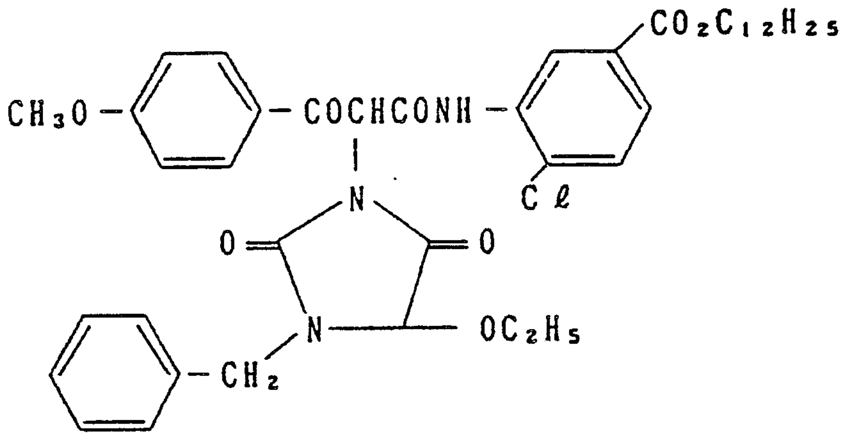

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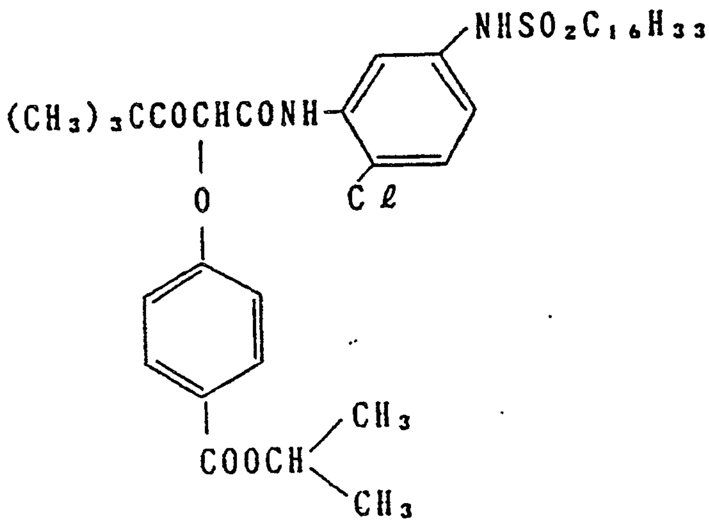

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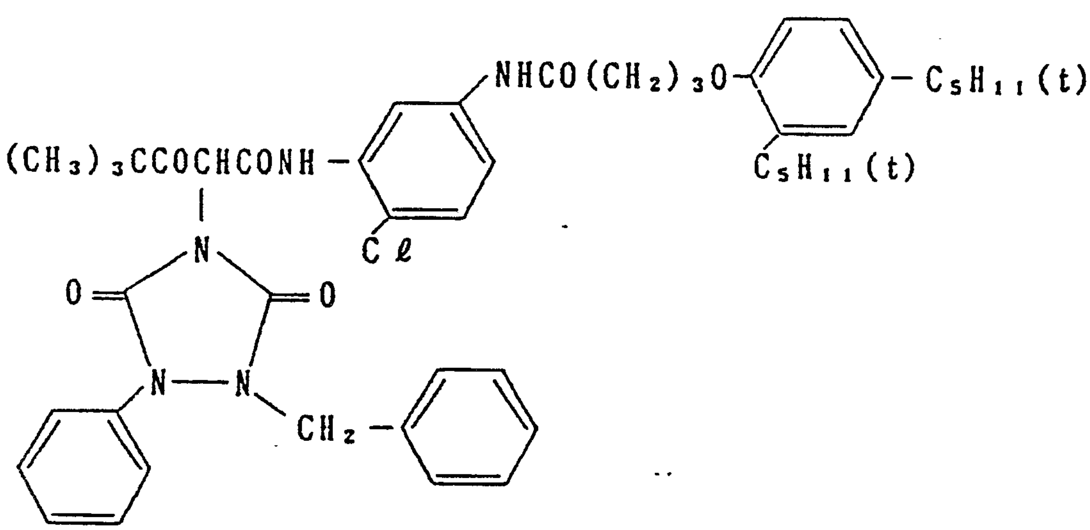

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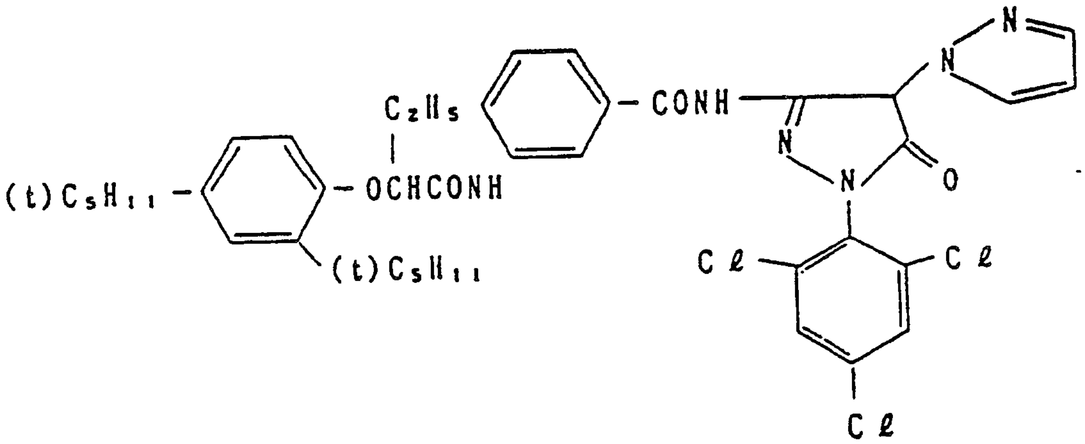

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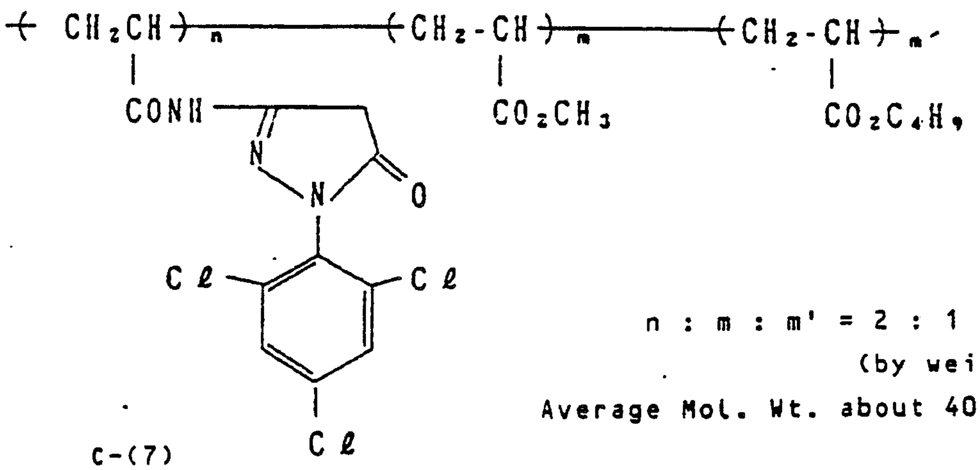
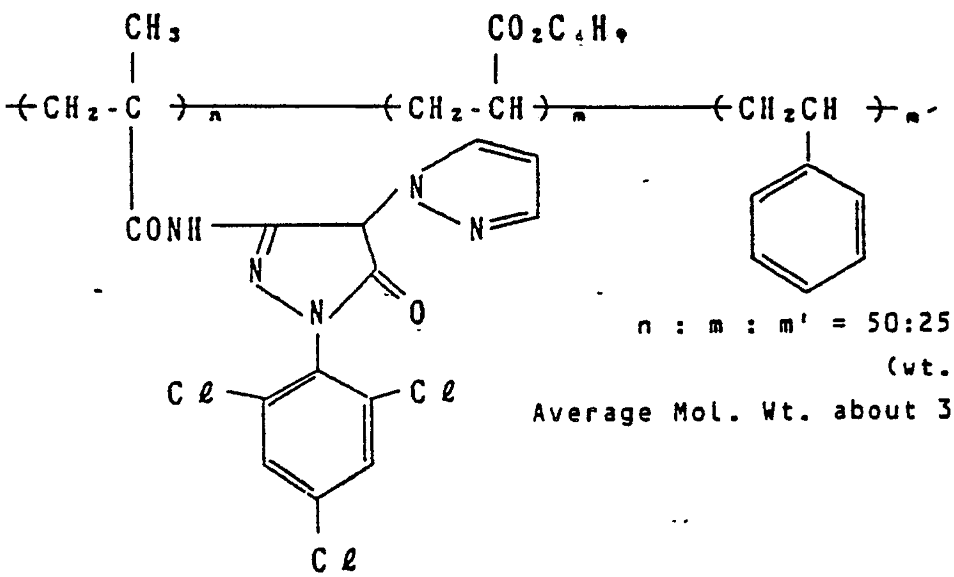


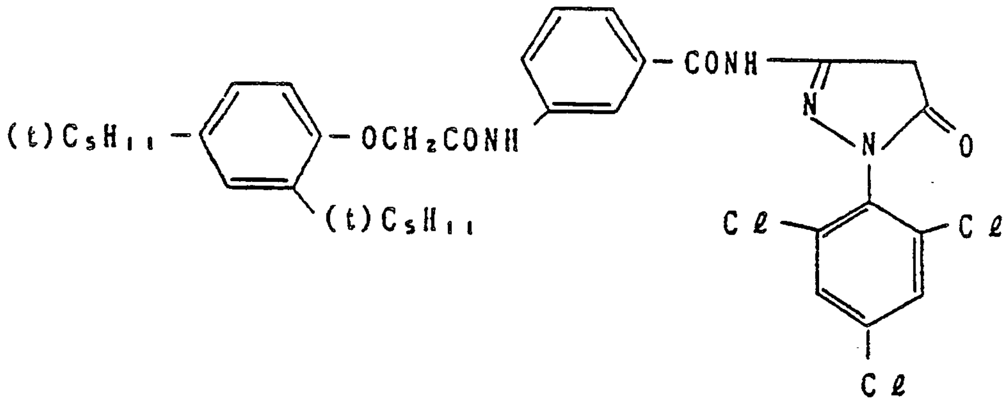
n : m : m' = 2 : 1 : 1
(by weight)
Average Mol. Wt. about 40,000

c-(7)



n : m : m' = 50:25:25
(wt.%)
Average Mol. Wt. about 30,000

C-(8)



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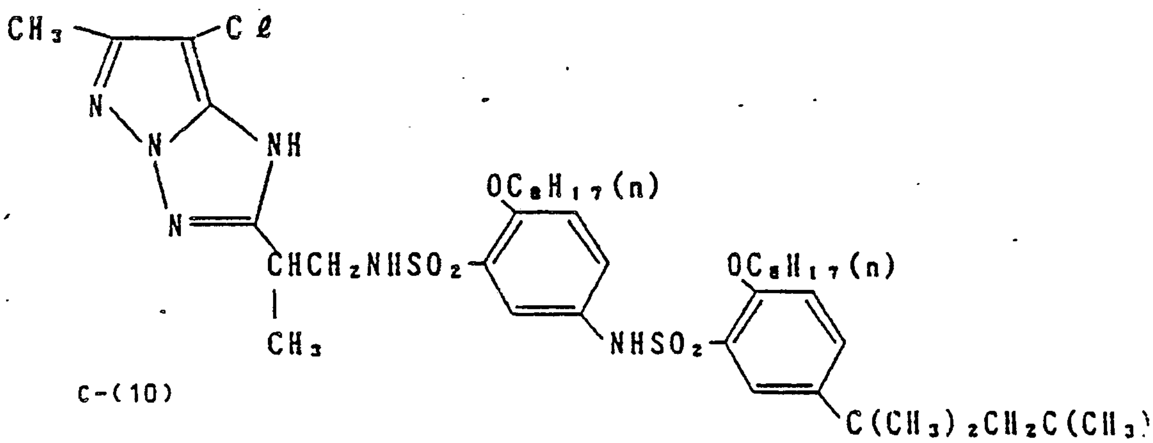

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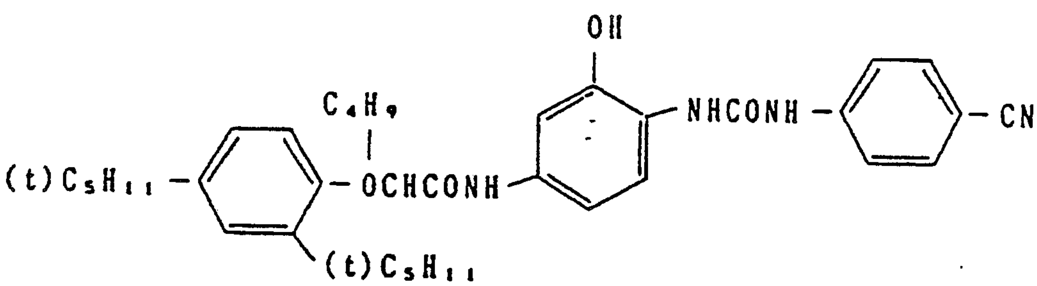

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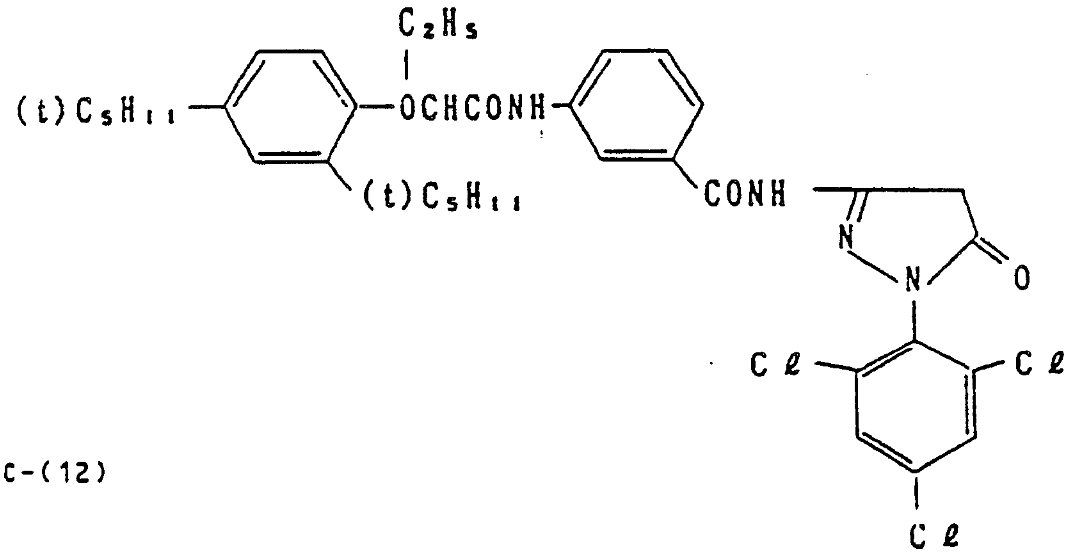

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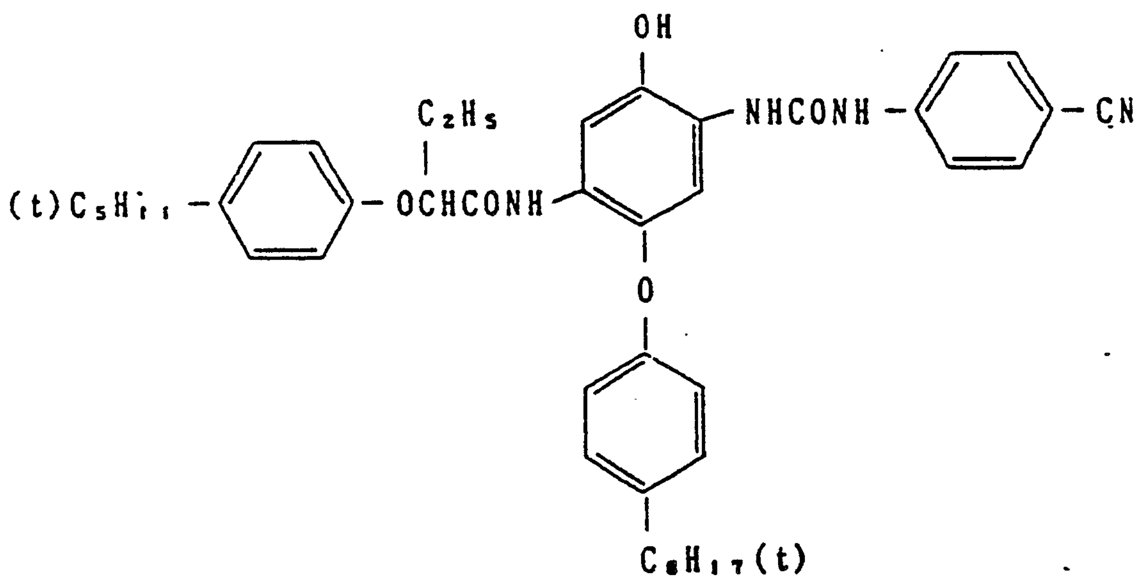

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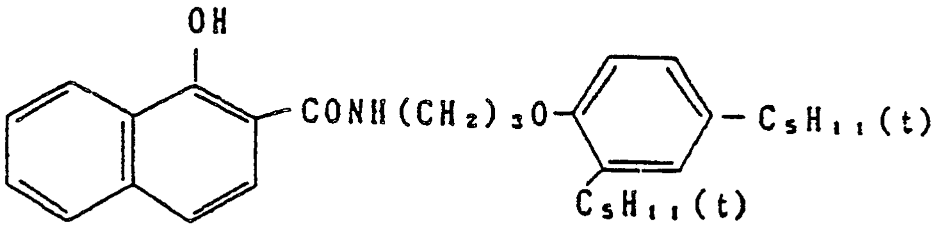

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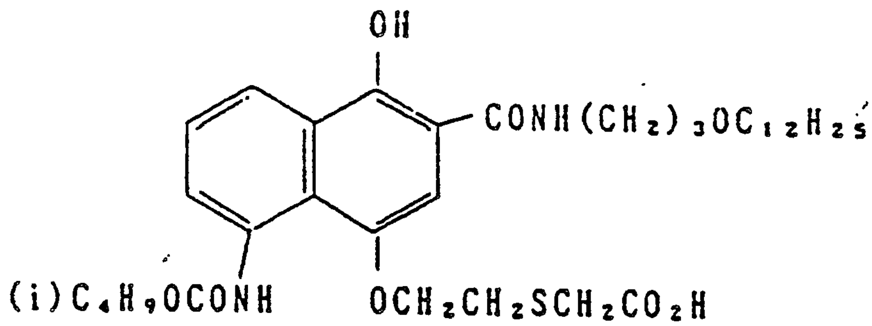

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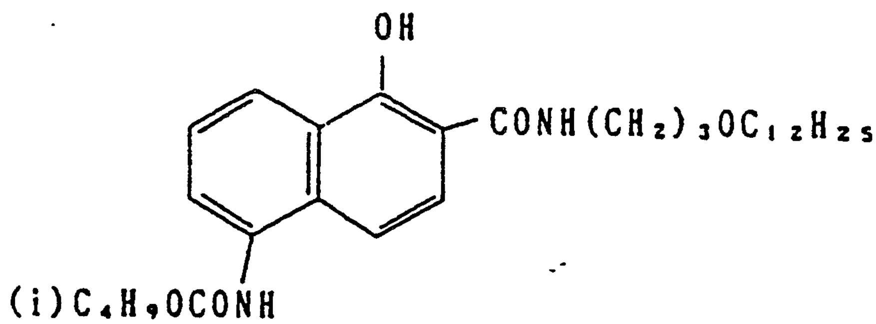

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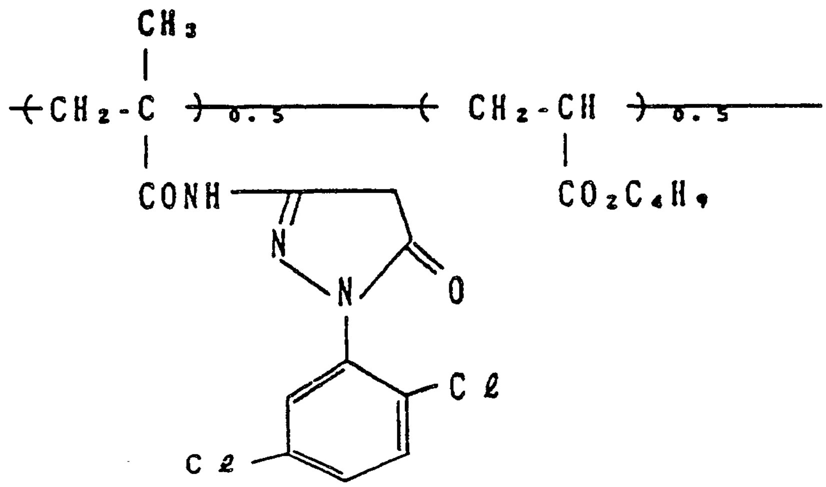

(Numbers signify ratio by weight)

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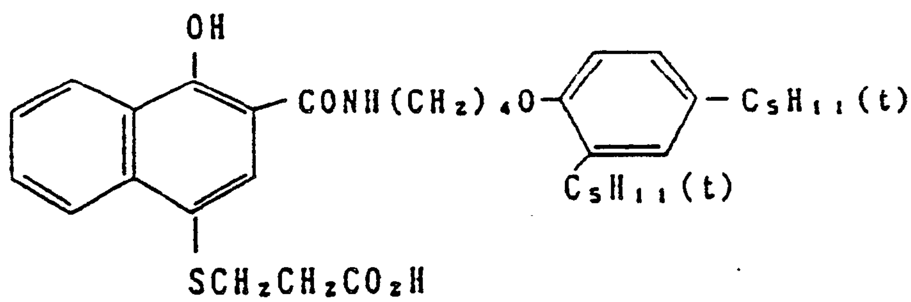

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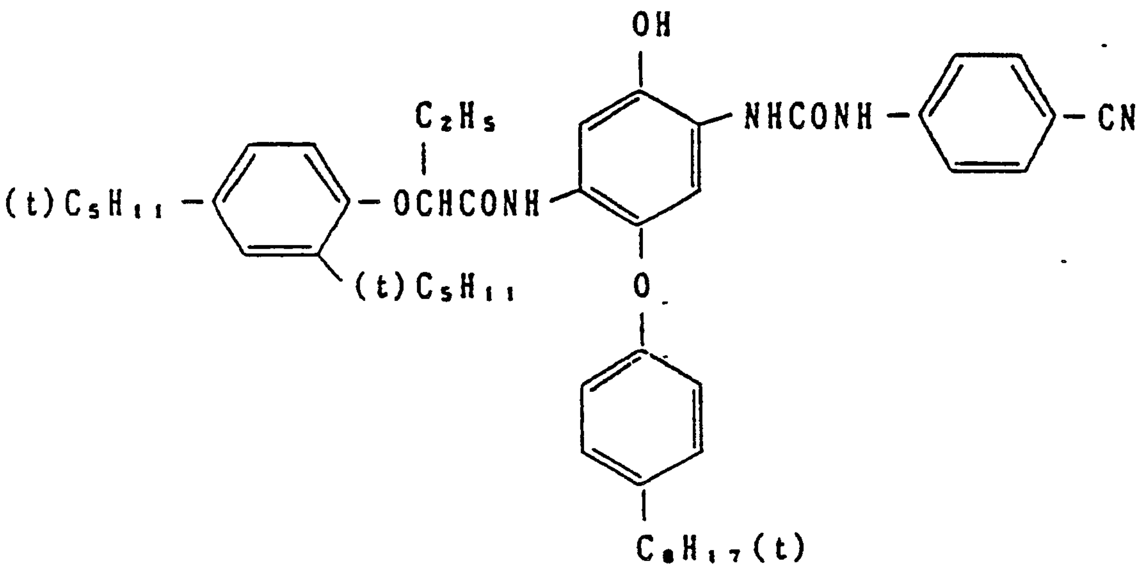

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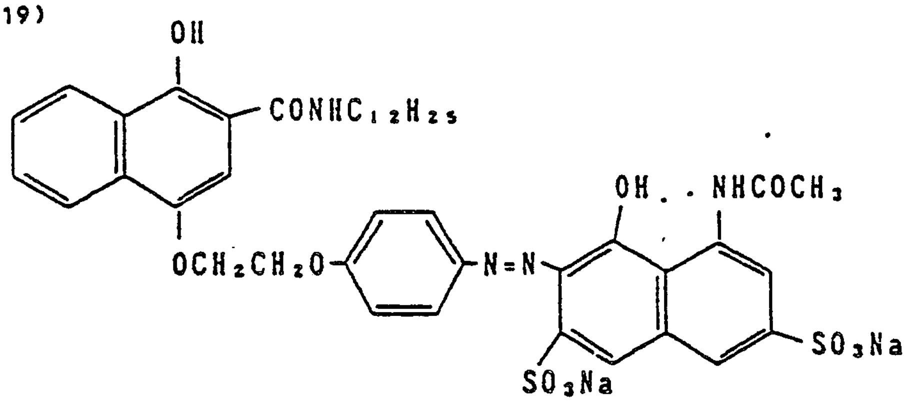
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SO3Na

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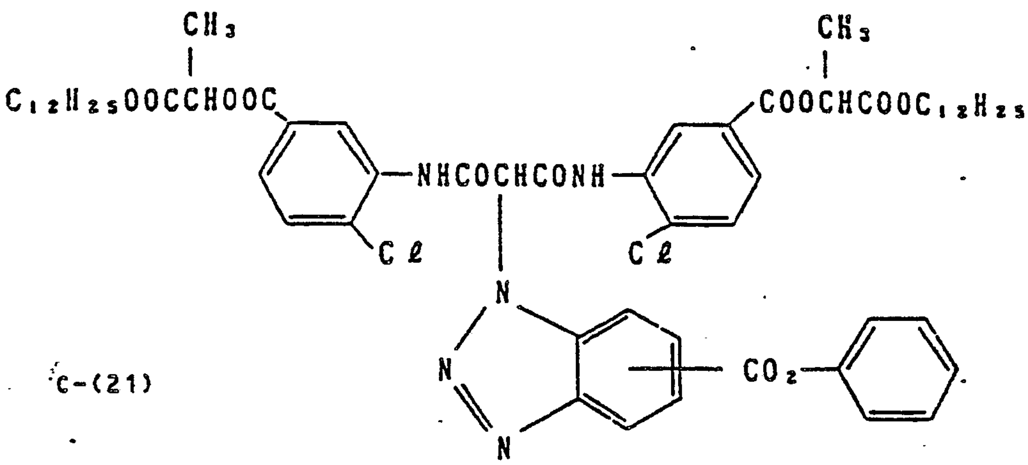
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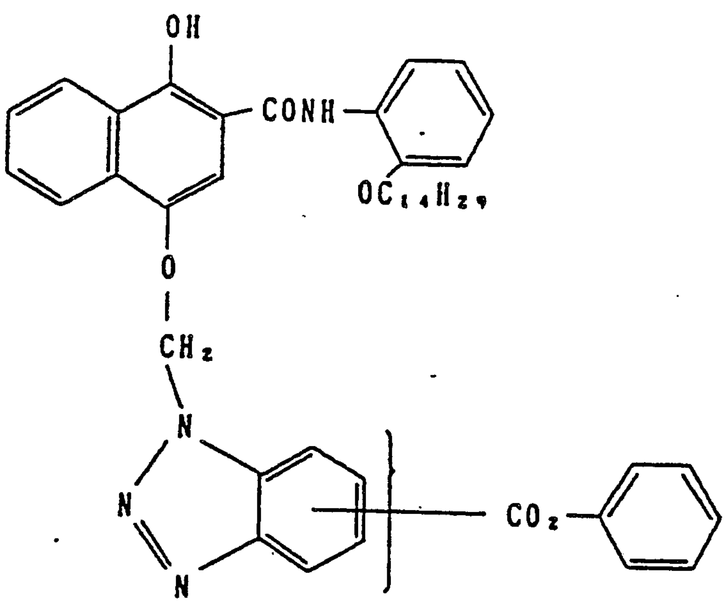
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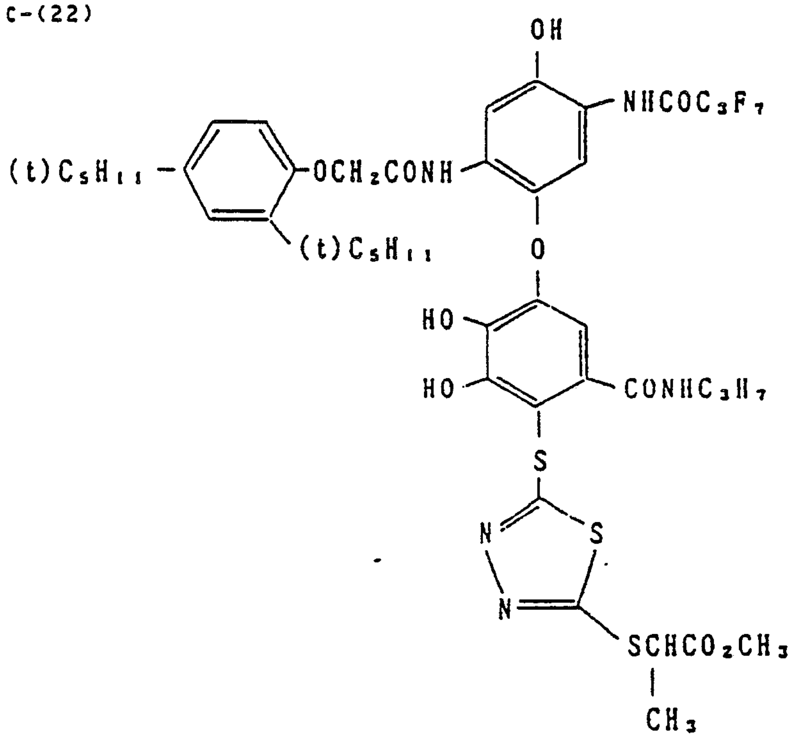
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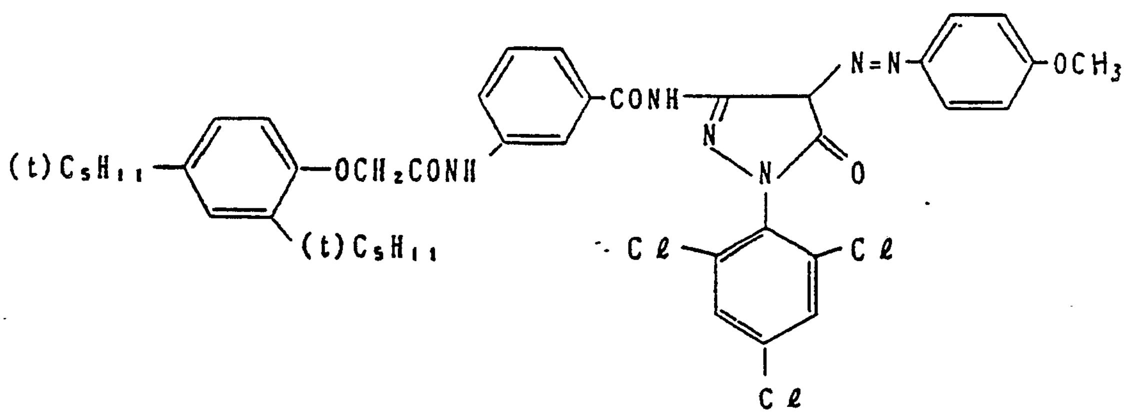
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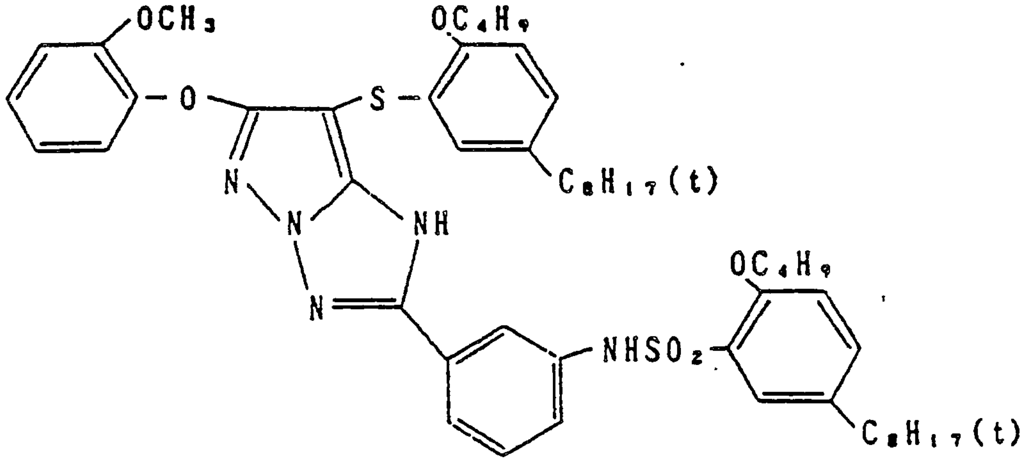
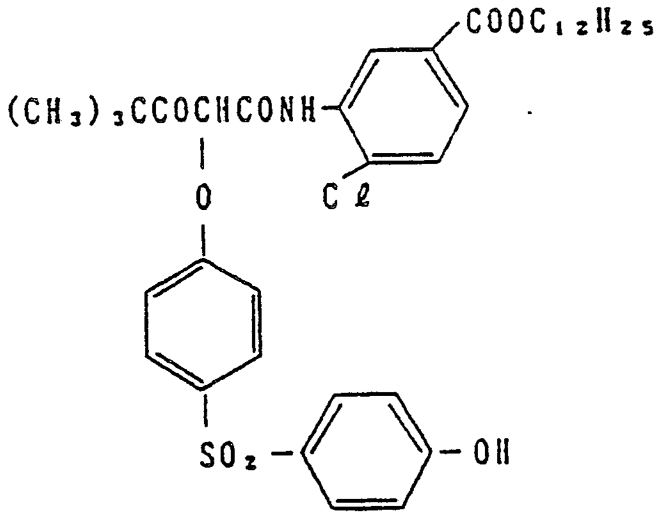
N
O
(t)C5H11
Cℓ
Cℓ
Cℓ

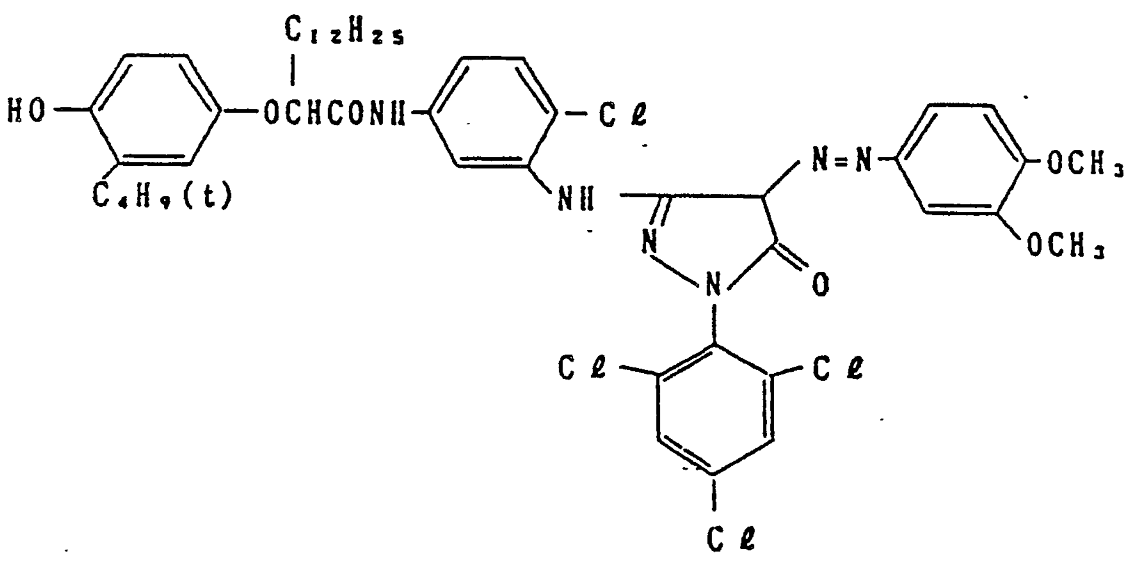
C-(24)


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

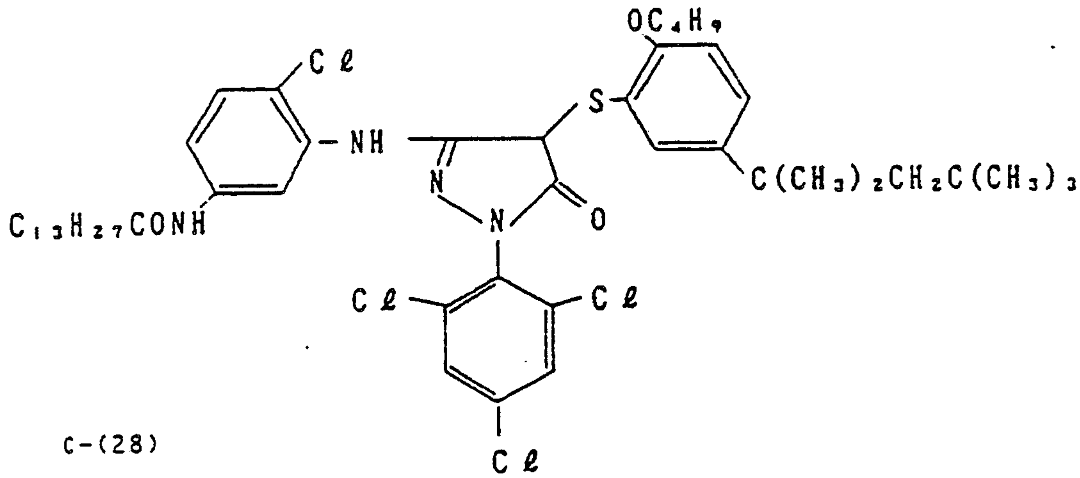
C-(25)


COOC₁₂H₂₅
(CH₃)₃CCOCHCONH
O
Cℓ
SO₂
OH

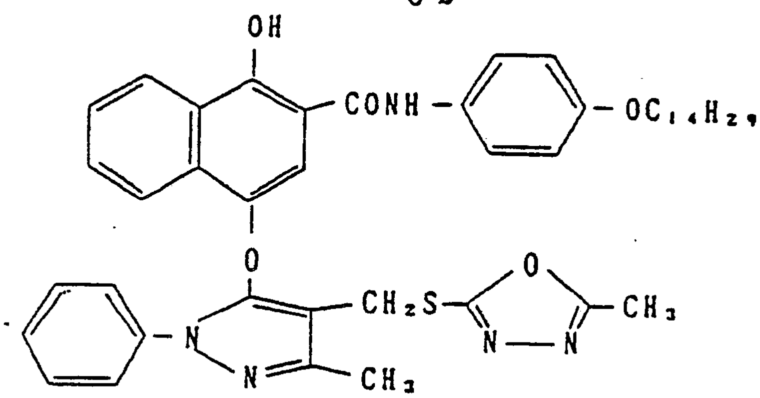
C-(26)


C₁₂H₂₅
HO
OCHCONH
Cℓ
C₄H₉(t)
NH
N=N
OCH₃
OCH₃
N
N
O
Cℓ
Cℓ
Cℓ

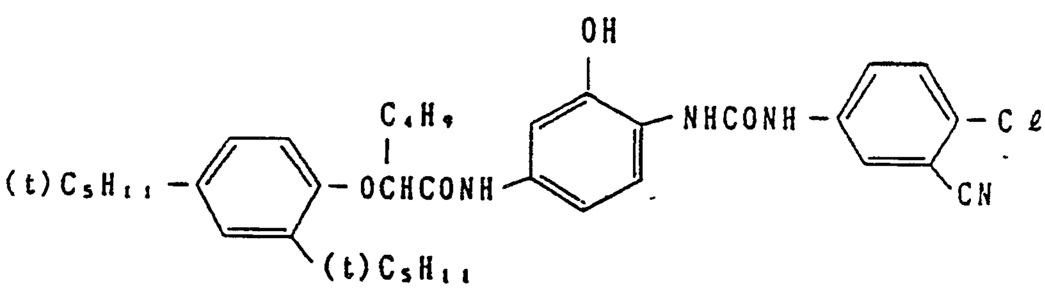
C-(27)



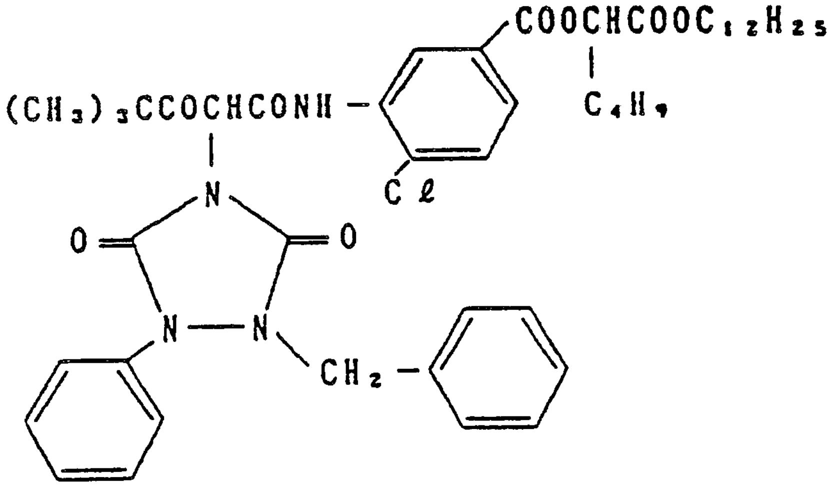
C-(28)



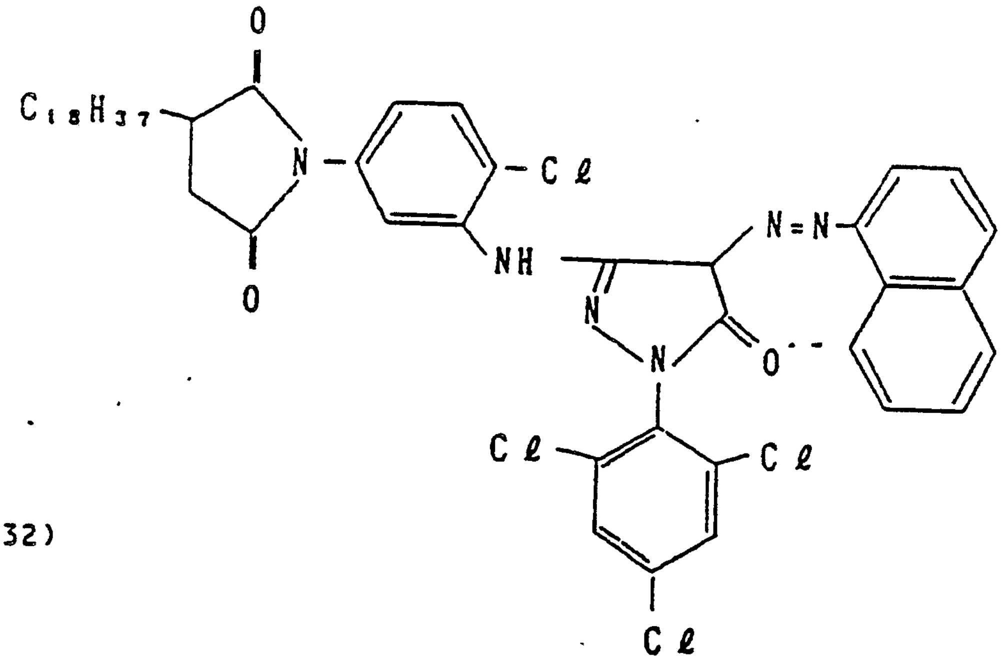
C-(29)



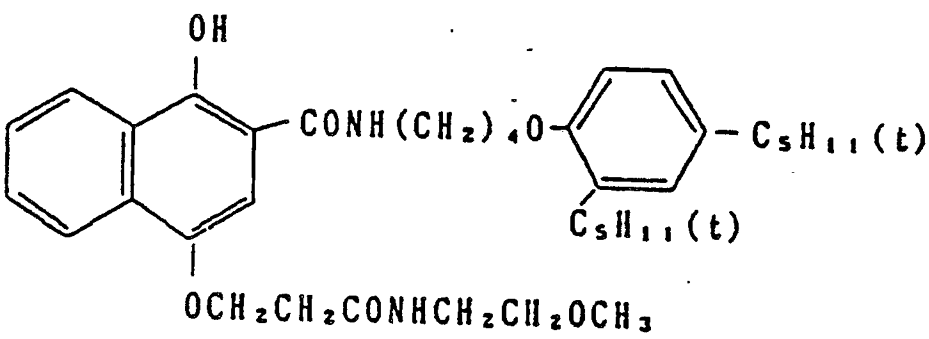
C-(30)



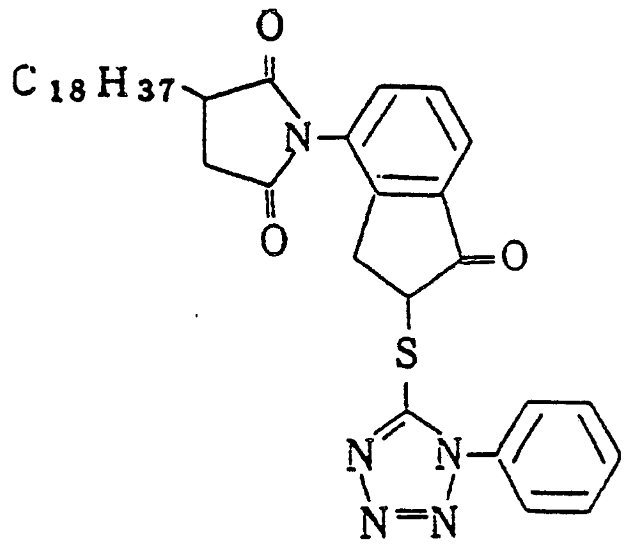
C-(31)



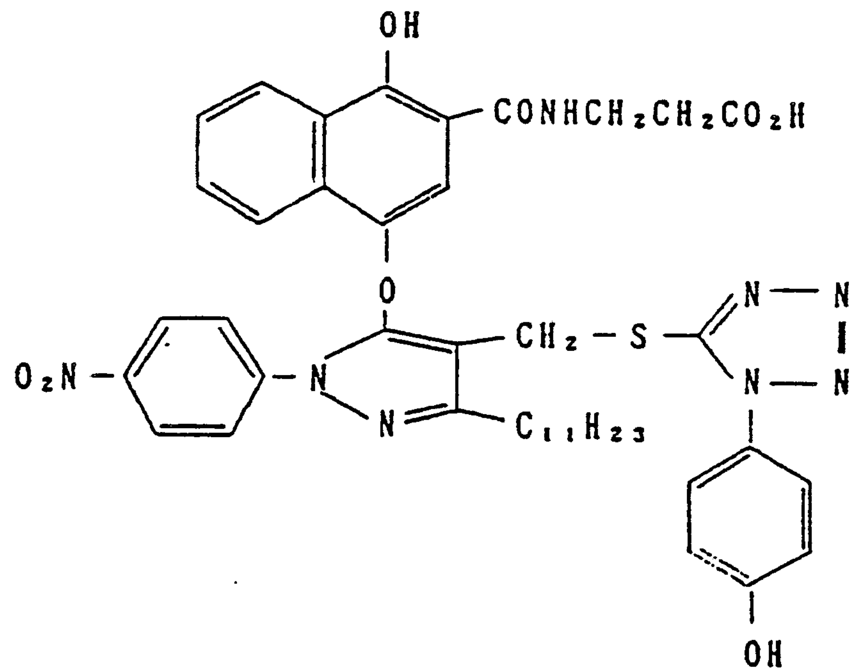
C-(32)



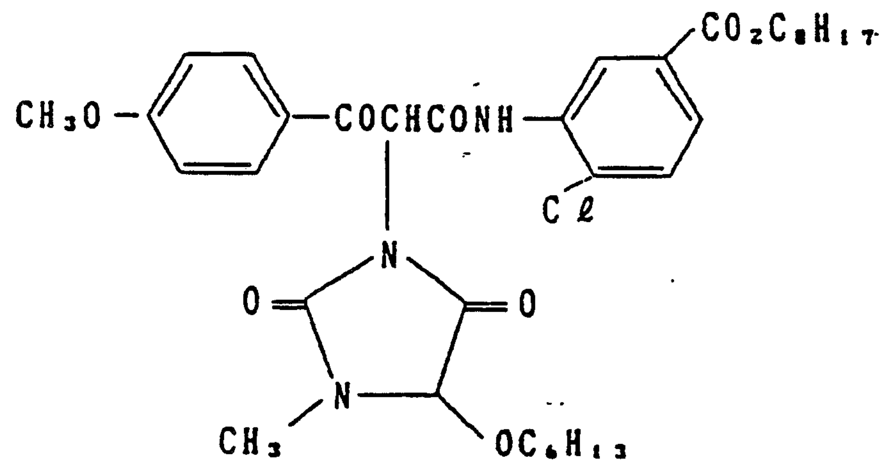
c-(33)


C18H37
O
N
O
O
S
N
N
N=N

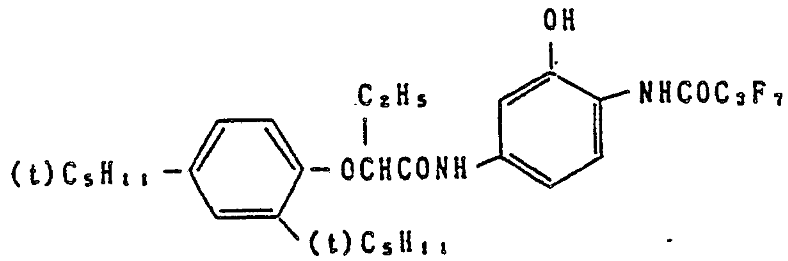
c-(34)


OH
CONHCH2CH2CO2H
O
O2N
N
CH2 - S
N — N
N — N
N
C11H23
OH

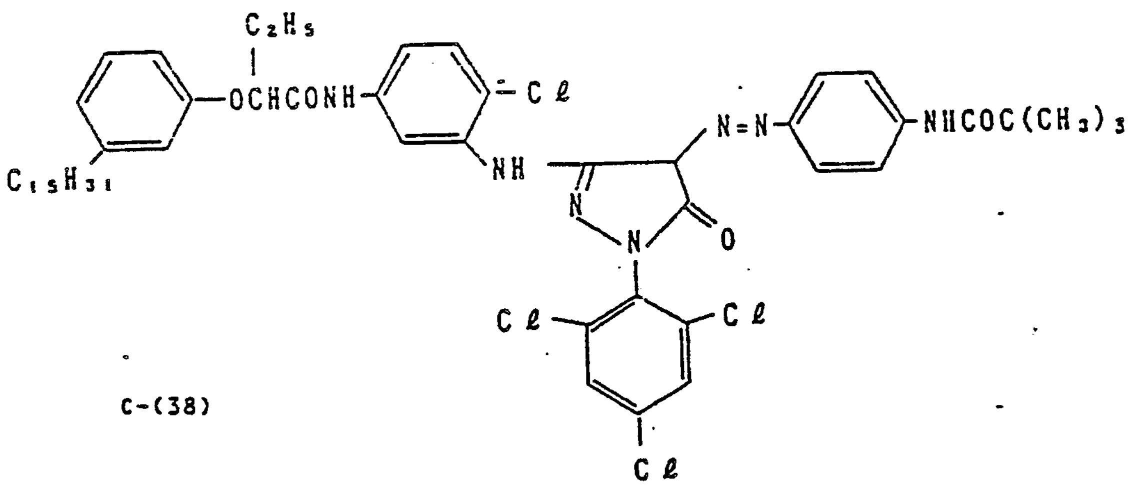
c-(35)


CO2C8H17
CH3O
COCHCONH
Cl
N
O
O
N
CH3
OC6H13

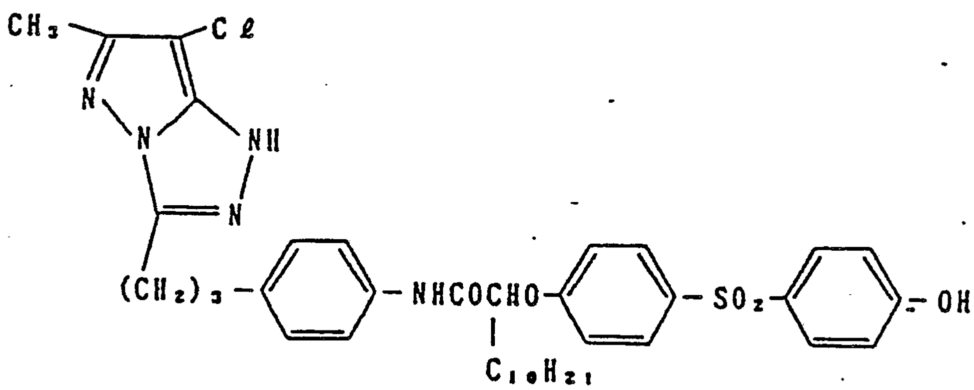
C-(36)



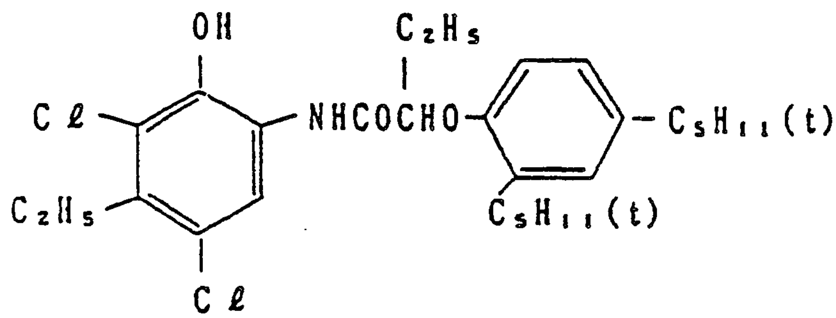
C-(37)



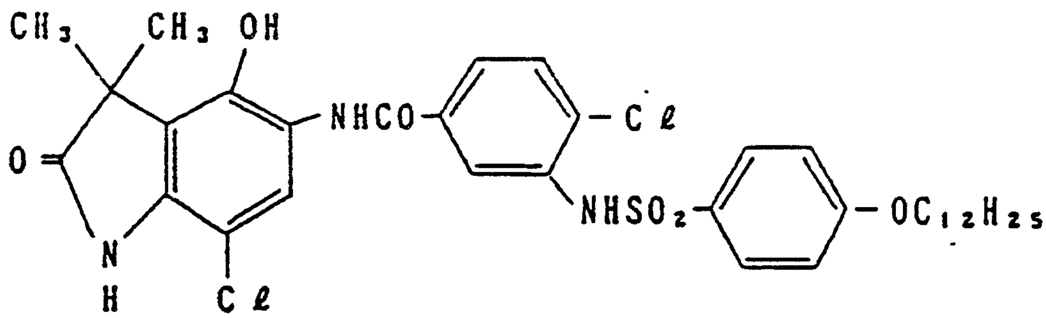
C-(38)



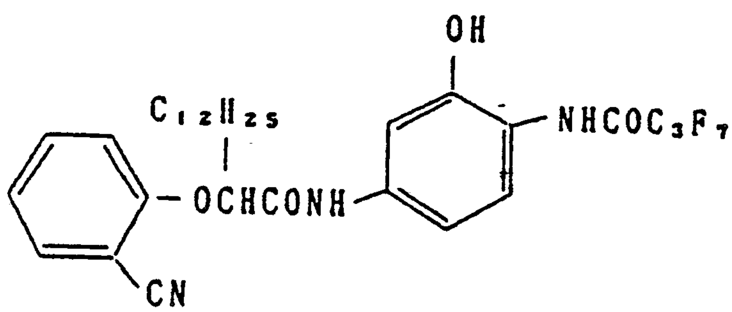
C-(39)



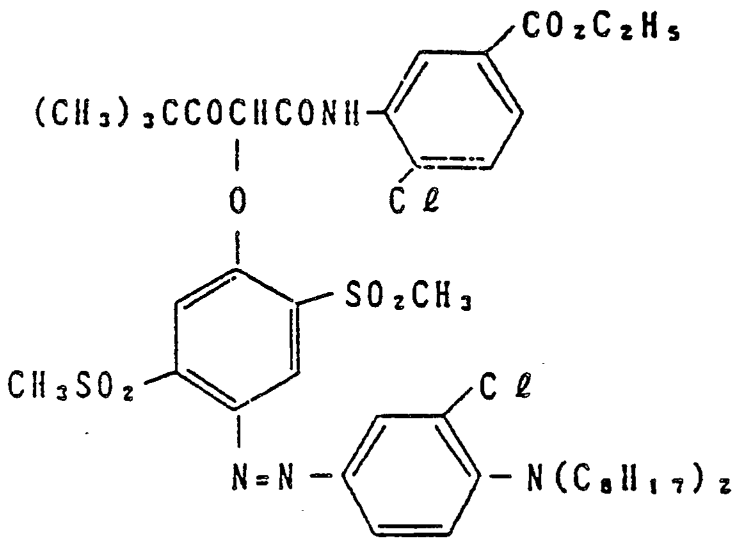
C-(40)



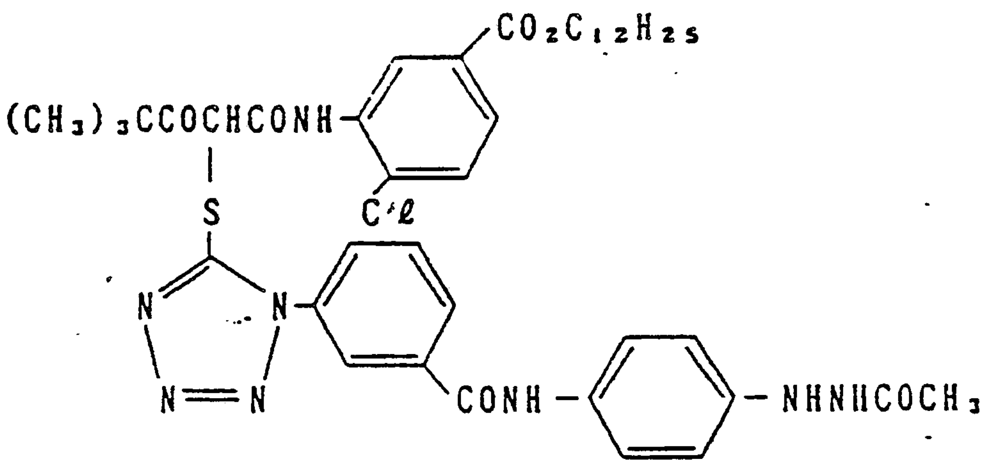
C-(41)



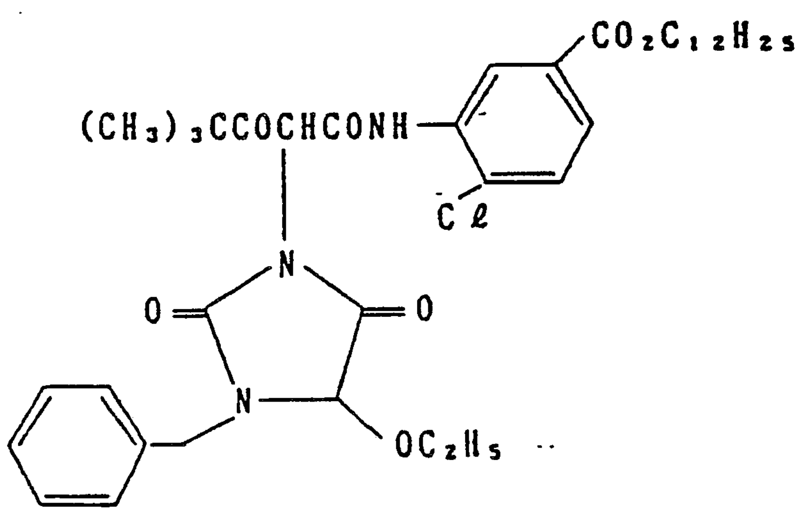
C-(42)



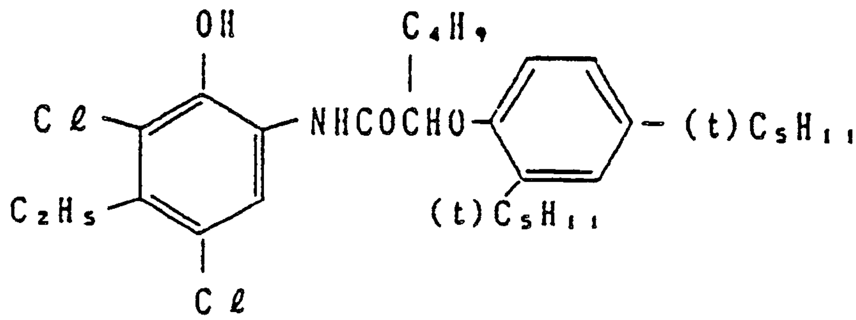
C-(43)



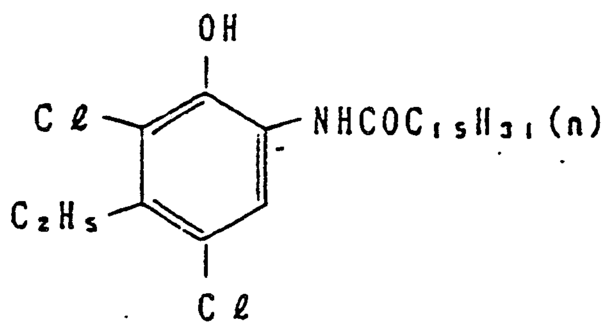
C-(44)



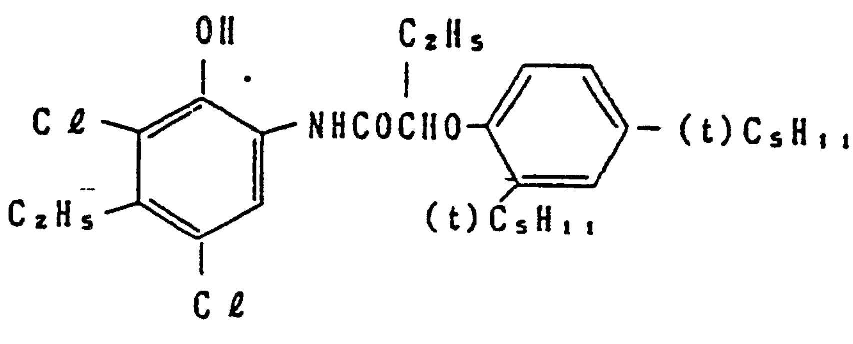
C-(45)


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

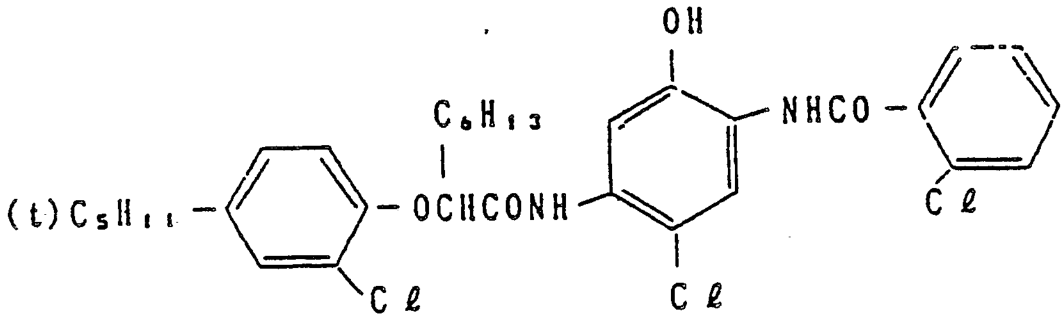
C-(46)


OH
Cl
NHCOC₁₅H₃₁(n)
C₂H₅
Cl

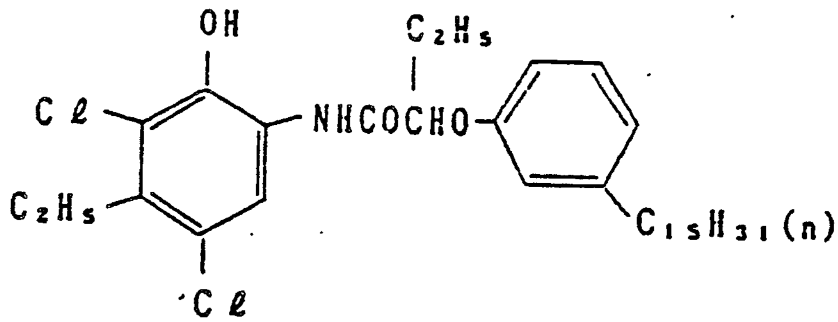
C-(47)


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

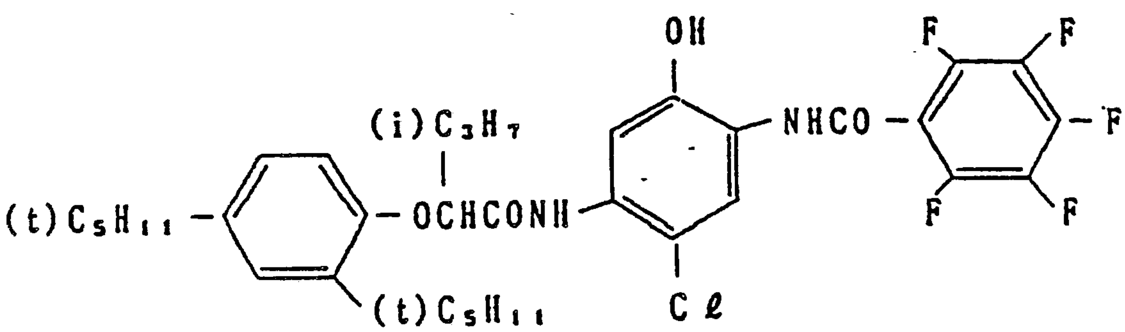
C-(48)


OH
C_6H_{13}
NHCO
$(t)C_5H_{11}$
OCHCONH
Cℓ
Cℓ
Cℓ

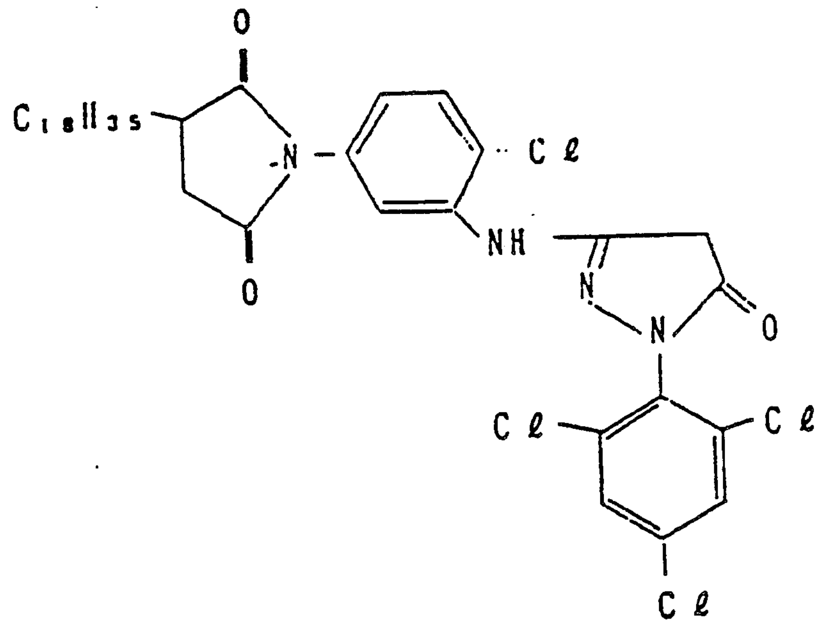
C-(49)


OH
C_2H_5
Cℓ
NHCOCHO
C_2H_5
$C_{15}H_{31}(n)$
Cℓ

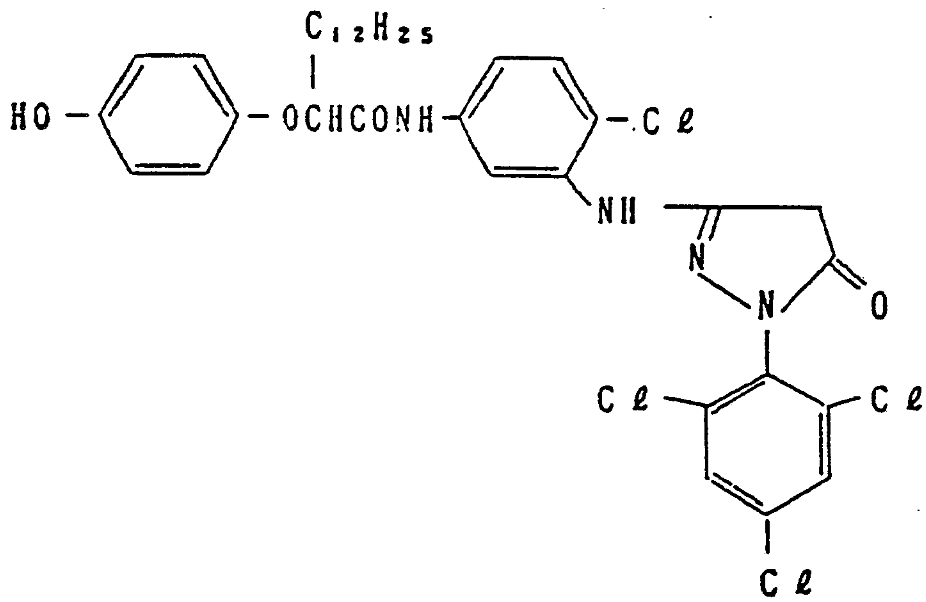
C-(50)


OH
F
F
$(i)C_3H_7$
NHCO
F
$(t)C_5H_{11}$
OCHCONH
F
F
$(t)C_5H_{11}$
Cℓ

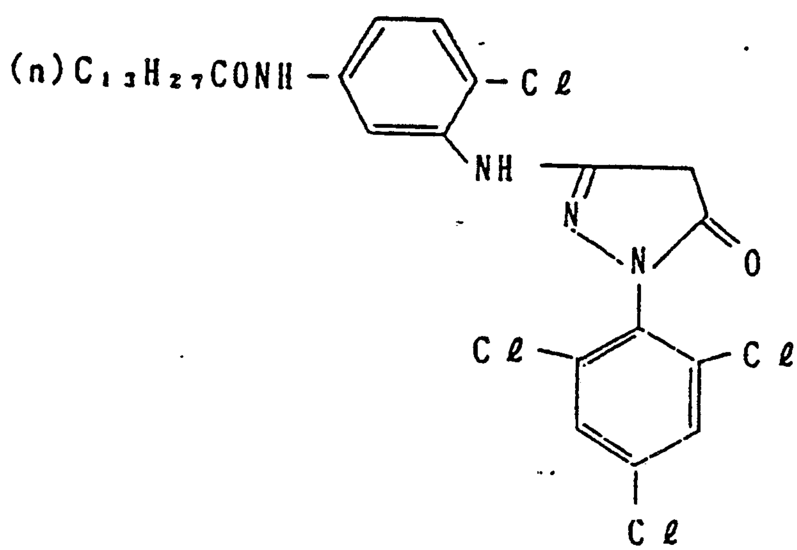
c-(51)


O
C₁₈H₃₅
N
Cℓ
NH
N
N
O
O
Cℓ
Cℓ
Cℓ

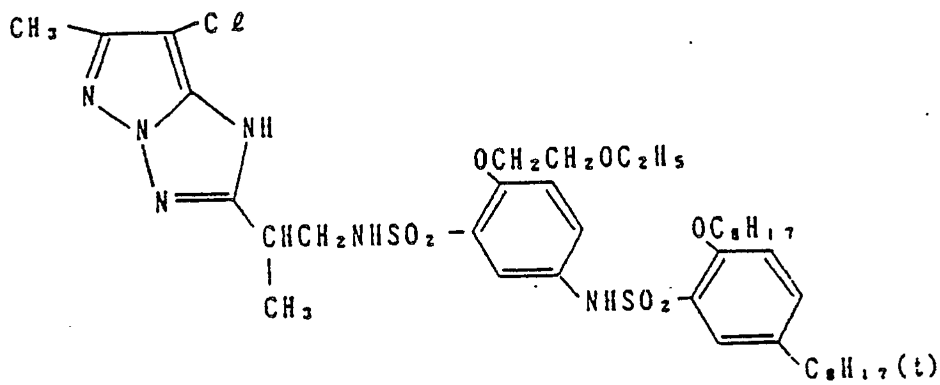
c-(52)


C₁₂H₂₅
HO
OCHCONH
Cℓ
NH
N
N
O
Cℓ
Cℓ
Cℓ

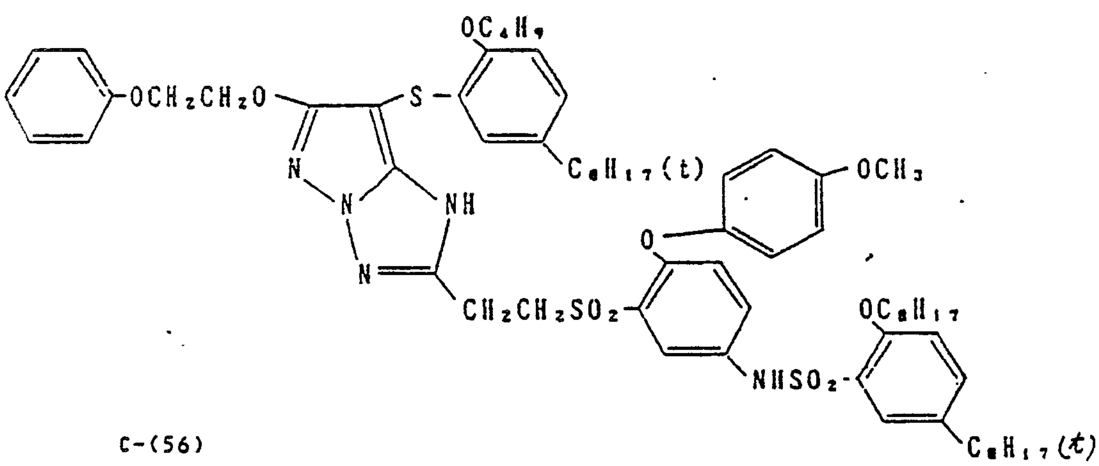
c-(53)


(n)C₁₃H₂₇CONH
Cℓ
NH
N
N
O
Cℓ
Cℓ
Cℓ

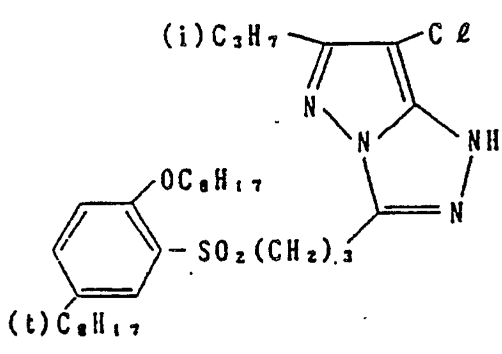
C-(54)


CH3
Cℓ
N
N
NH
N
OCH2CH2OC2H5
CHCH2NHSO2
CH3
OC8H17
NHSO2
C8H17(t)

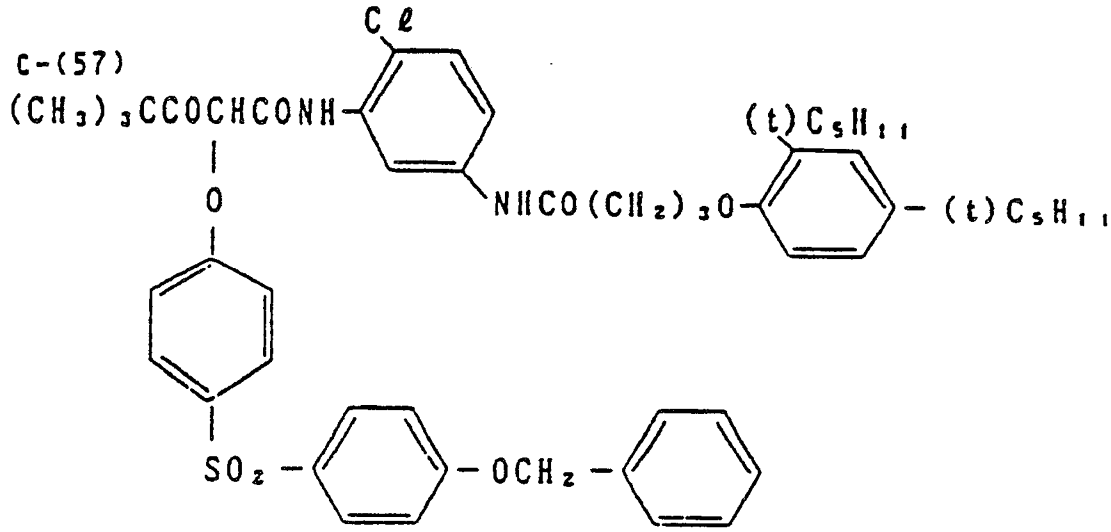
C-(55)


OC4H9
OCH2CH2O
S
N
N
NH
N
C8H17(t)
OCH3
O
CH2CH2SO2
OC8H17
NHSO2
C8H17(t)

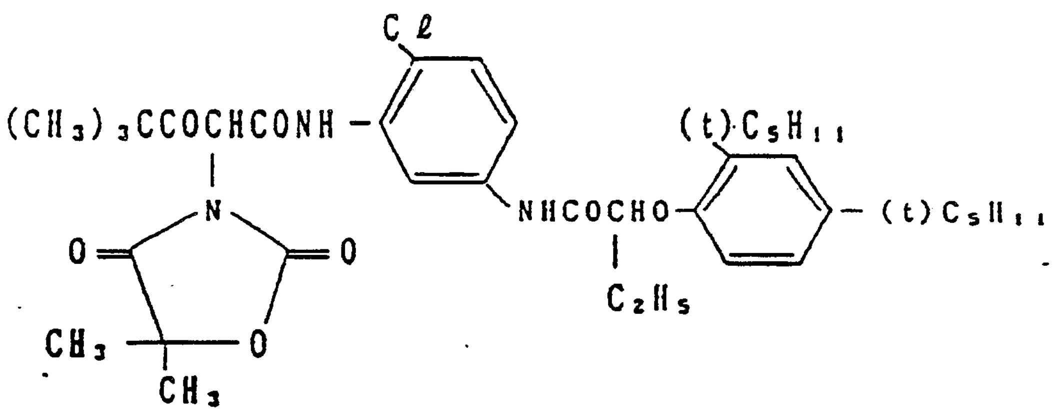
C-(56)


(i)C3H7
Cℓ
N
N
NH
N
OC8H17
SO2(CH2)3
(t)C8H17

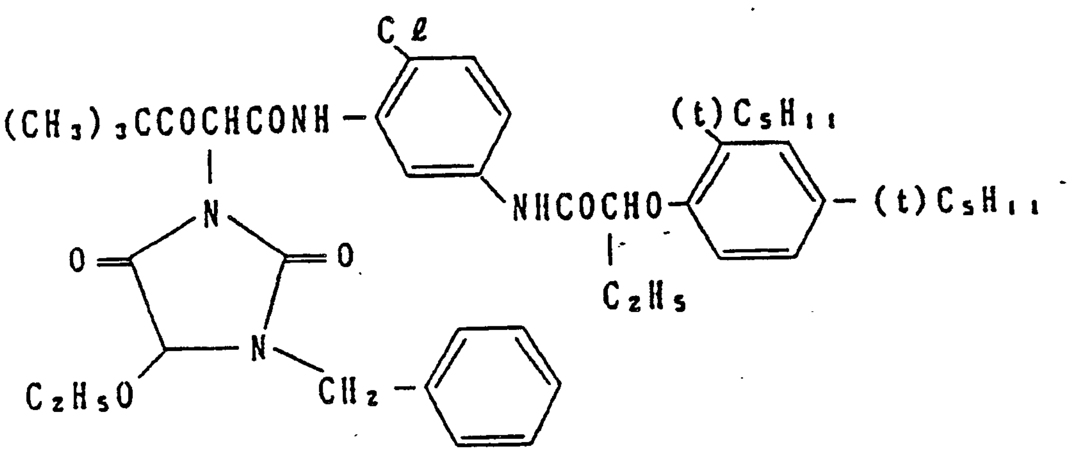
c-(57)



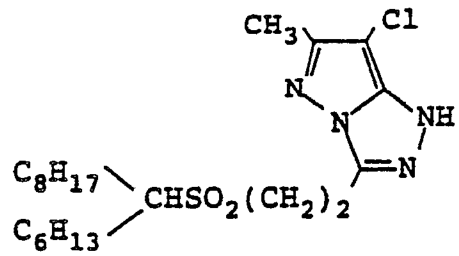
c-(58)



c-(59)



C-(60)



The couplers which are uSed in the invention can be introduced into the light sensitive materials using various known methods of dispersion.

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

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

The processes and effects of the latex dispersion method and actual examples of latexes for impregnation purposes have been disclosed in U.S. Patent 4,199,363, and in DE-A-2,541,247 and 2,541,230.

The invention can be applied to various color photosensitive materials. Typical examples include color negative films for general purposes or for cinematographic purposes, color reversal films for slides or television purposes, color papers, color positive films and color reversal papers.

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

Color photographic materials to which the invention has been applied can be developed and processed using the normal methods disclosed on pages 28 and 29 of the aforementioned Research Disclosure, No. 17643 and from the left hand column to the right hand column of page 651 of Research Disclosure, No. 18716.

The color development bath used for the development processing of photosensitive materials of this invention is preferably an aqueous alkaline solution which contains a primary aromatic amine based color developing agent as the principal component. Aminophenol based compounds are also useful as color developing agents, but the use of p-phenylenediamine based compounds is preferred. Typical examples of these compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino N-ethyl N-β-hydroxyethylaniline, 3- methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline 3-methyl 4-amino-N-ethyl-N-β-methoxyethylaniline and the sulfate, hydrochloride and p-toluenesulfonate salts of these compounds. Two or more of these compounds can be used conjointly, depending on the intended purpose.

The color development baths generally contain pH buffers, such as the carbonates, borates or phosphates of the alkali metals, and development inhibitors or anti-fogging agents such as bromides, iodides, benzimidazoles, benzothiazoles or mercapto compounds etc. They may also contain, as required, various preservatives, such as hydroxylamine, diethylhydroxylamine, sulfites, hydrazines, phenylsemicarbazides, triethanolamine, catechol sulfonic acids, triethylenediamine(1,4-diazabicyclo[2,2,2]octane) etc., organic solvents such as ethylene glycol and diethylene glycol, development accelerators such as benzyl alcohol, poly(ethylene glycol), quaternary ammonium salts and amines, color forming couplers, competitive couplers, fogging agents such as sodium borohydride, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, viscosity imparting agents, various chelating agents as typified by the aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, typical examples of which include ethylenediamine tetra-acetic acid, nitrilo triacetic acid, diethylenetriamine penta-acetic acid, cyclohexanediamine tetra-acetic acid, hydroxyethylimino diacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N′,N′-tetramethylenephosphonic acid, ethylenediamine di(o-hydroxyphenylacetic acid), and salts of these compounds.

Color development is carried out after normal black and white development in the case of reversal processing. The known black and white developing agents, for example the dihydroxybenzenes such as hydroquinone, the 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, and the amino phenols such as N-methyl-p-aminophenol, can be used individually or in combinations in the black and white development bath.

The pH of these color development baths and black and white development baths is generally within the range from 9 to 12. Furthermore, the replenishment rate of the development bath depends on the color photographic material which is being processed, but it is generally not more than 3 liters per square meter of photosensitive material and it is possible, by reducing the bromide ion concentration in the replenisher, to use a replenishment rate of not more than 500 ml per square meter of photosensitive material. The prevention of loss of liquid by evaporation, and aerial oxidation, by minimizing the contact area with the air in the processing tank is desirable in cases where the replenishment rate is low. Furthermore, the replenishment rate can be reduced by using a means of suppressing the accumulation of bromide ion in the development bath.

The photographic emulsion layers are subjected to a normal bleaching process after color development. The bleaching process may be carried out at the same time as the fixing process (in a bleach-fix process) or it may be carried out as a separate process. Moreover, a bleach-fix process can be carried out after a bleach process in order to speed-up processing. Moreover processing can be carried out in two connected bleach-fix baths, a fixing process can be carried out before carrying out a bleach-fix process, or a bleaching process can be carried out after a bleach-fix process, according to the intended purpose of the processing. Compounds of a poly-valent metal such as iron(III), cobalt(III), chromium(VI), copper(II), peracids, quinones, nitro compounds can be used as bleaching agents. Typical bleaching agents include ferricyanides; dichromates; organic complex salts of iron(III) or cobalt(III), for example complex salts with aminopoly carbcxylic acids such as ethylenediamine tetra-acetic acid, diethylenetriamine penta-acetic acid, cyclohexanediamine tetra-acetic acid, methylimino diacetic acid, 1,3-diaminopropane tetra-acetic acid, glycol ether diamine tetra-acetic acid, or citric acid, tartaric acid, malic acid; persulfates; bromates; permanganates and nitrobenzenes. Of these materials, the use of the aminopolycarboxylic acid iron(III) complex salts, principally ethylenediamine tetra-acetic acid iron(III) complex salts, and persulfates is preferred from the points of view of both rapid processing and the prevention of environmental pollution. Moreover, the amino polycarboxylic acid iron(III) complex salts are especially useful in both bleach baths and bleach-fix baths. The pH of a bleach or bleach-fix beth in which aminopolycarboxylic acid iron(IIII) complex salts are being used is normally from 5.5 to 8, but a lower pH can be used in order to speed-up processing.

Bleach accelerators can be used, as required, in the bleach baths, bleach-fix baths, or bleach or bleach-fix pre-baths. Actual examples of useful bleach accelerators have been disclosed in the following specifications: Thus there are the compounds which have a mercapto group or a disulfide group disclosed in U.S. Patent 3,893,858, West German Patent Nos. 1,290,812 and 2,059,988, JP-A-53-32736 JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426, and in Research Disclosure No. 17129 (July 1978) etc.; the thiazolidine derivatives disclosed in JP-A-50-140129; the thiourea derivatives disclosed in JP-B-45-8506, JP-A-52-20832 and JP-A-53-32735, and in U.S. Patent 3,706,561; the iodides disclosed in West German Patent 1,127,715 and in JP A-58-16235; the polyoxyethylene compounds disclosed in West German Patents 966,410 and 2,748,430; the polyamine compounds disclosed in JP-B-45-8836; the other compounds disclosed in JP-A-49-42434, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506 and JP-A-58-163940; and bromide ions etc. Among these compounds, those which have a mercapto group or a disulfide group are preferred in view of their large accelerating effect, and the use of the compounds disclosed in U.S. Patent 3,893,858, West German Patent 1,290,812, and in JP-A-53-95630 is especially desirable. Moreover, the use of the compounds disclosed in U.S. Patent 4,552,834 is also desirable. These bleach accelerators may be added to the sensitive material. These bleach accelerators are especially effective when bleach-fixing color photosensitive materials for photographic purposes.

Thiosulfates, thiocyanates, thioether based compounds, thioureas and large quantities of iodide etc. can be used as fixing agents, but thiosulfates are generally used for this purpose, and ammonium thiosulfate in particular can be used in the widest range of applications. Sulfites, bisulfites, or carbonylbisulfite addition compounds, are preferred as preservatives for bleach-fix baths.

The silver halide color photographic materials of this invention are generally subjected to a water washing and/or stabilizing process after the desilvering process. The amount of water used in the water washing process can be fixed within a wide range according to the nature of the photosensitive material (for example the materials, such as the couplers, which are being used), the wash water temperature, the number of washing tanks (the number of washing stages), the replenishment system, i.e. whether a counter-flow or a sequential-flow system is used, and various other conditions. The relationship between the amount of water used and the number of water washing tanks in a multi-stage counter-flow system can be obtained using the method outlined on pages 248 to 253 of the Journal of the Society of Motion Picture and Television Engineers, Volume 64 (May 1955).

The amount of wash water can be greatly reduced by using the multi-stage counter-flow system noted in the aforementioned literature, but bacteria proliferate due to the increased residence time of the water in the tanks and problems arise as a result of the sediments which are formed becoming attached to the photosensitive material. The method in which the calcium ion and manganese ion concentrations are reduced as disclosed in Japanese Patent Application No. 61-131632 can be used very effectively to overcome problems of this sort in the processing of color photosensitive materials of this invention. Furthermore, the isothiazolone compounds and thiabendazoles disclosed in JP-A 57-8542 and chlorine based disinfectants such as chlorinated sodium isocyanurate, and benzotriazoles etc., and the disinfectants disclosed in Chemistry of Biocides and Fungicides by Horiguchi, (Reduction of Micro-organisms, Biocidal and Fungicidal Techniques), published by the Health and Hygiene Technical Society and in A Dictionary of Biocides and Fungicides, published by the Japanese Biocide and Fungicide Society, can be used for this purpose.

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

Furthermore, there are cases in which a stabilization process is carried out following the aforementioned water washing process, and the stabilizing baths which contain formalin and surfactant which are used as a final bath for color photosensitive materials used for photographic purposes are an example of such a process. Various chelating agents and fungicides etc. can be added to these stabilizing baths.

The overflow which accompanies replenishment of the above mentioned wash water and/or stabilizer can be re-used in other processes such as the desilvering process etc.

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

Various 1-phenyl-3-pyrazolidones can be incorporated, as required, into the silver halide color photosensitive materials of this invention with a view to accelerating color development. Typical compounds of this type have been disclosed in JP-A-56-64339, JP-A-57-144547 and JP-A-58-115438 etc.

The various processing baths are used at a temperature of from 10 to 50 °C in this invention. The standard temperature is normally from 33 to 38 °C, but processing is accelerated and the processing time is shortened at higher temperatures and, conversely, increased picture quality and improved stability of the processing baths can be achieved at lower temperatures. Furthermore, processes using hydrogen peroxide intensification or cobalt intensification as disclosed in West German Patent 2,226,770 or U.S. Patent 3,674,499 can be carried out in order to economize on silver in the photosensitive material.

Furthermore, silver halide photosensitive materials of this invention can also be used as the heat developable photosensitive materials disclosed in U.S. Patents 4,500,626, JP-A-60-133,449, JP-A-59-218443 and JP-A-61-238056, and in EP-A-210,660A2 etc.

The invention is described in detail below by means of examples, but the invention is not limited by these examples. Unless otherwise indicated, all parts, percent. and ratios are by weight.

EXAMPLE 1

A color photographic material was prepared by the lamination coating of the first to the fourteenth layers indicated below on a triacetate base.

Photosensitive Layer Composition

The components and the amounts coated in units of grams per square meter are shown below.

First Layer (Anti-halogen Layer)

Black colloidal silver	0.30
Gelatin	2.50
UV-1	0.05
UV-2	0.10
UV-3	0.10
Solv-1	0.10

Second Layer (Intermediate layer)

Gelatin	0.50

Third Layer (Low speed Red Sensitive Layer)

Mono-disperse silver iodobromide emulsion (AgI 4 mol%, Cubic, Average grain size 0.3 μm, s/r=0.15)	0.50
ExS-1	1.40×10^{-3}
ExS-2	6.00×10^{-5}
Gelatin	0.80
Coupler (IV) of this invention	0.3
Solv-2	0.03

Fourth Layer (Medium Speed Red Sensitive Layer)

Mono-disperse silver iodobromide emulsion (AgI 2.5 mol%, Tetradecahedral, Average grain size 0.45 μm, s/r=0.15)	0.50
ExS-1	1.60×10^{-3}
ExS-2	6.00×10^{-5}
Gelatin	1.00
Coupler (IV) of this invention	0.45
Solv-2	0.05

Fifth Layer (High Speed Red Sensitive Layer)

Mono-disperse silver iodobromide emulsion (AgI 2.5 mol%, Tetradecahedral, Average grain size 0.60 μm, s/r=0.15)	0.30
ExS-1	1.60×10^{-3}
ExS-2	6.00×10^{-5}
Gelatin	0.70
Coupler (IV) of this invention	0.3
Solv-2	0.03

Sixth Layer (Intermediate Layer)

Gelatin	1.0
Cpd-1	0.1
Solv-1	0.03
Solv-2	0.08
Solv-3	0.12
Cpd-2	0.25

Seventh Layer (Low Speed Green Sensitive Layer)

Silver iodobromide emulsion (AgI=3.0 mol%, Regular crystal, twinned crystal mixture, Average grain size 0.3 μm)	0.65
ExS-3	3.30×10^{-3}
ExS-4	1.50×10^{-3}
Gelatin	1.50
ExM-1	0.10
ExM-2	0.25
Solv-2	0.30

Eighth Layer (High Speed Green Sensitive Layer)

Tabular silver iodobromide emulsion (AgI=2.5 mol%, Grains with a diameter/thickness ratio of at least 5 accounted for 50% of the projected area of all the grains, Average thickness of grains 0.15 μm)	0.70
ExS-3	1.30×10^{-3}
ExS-4	5.00×10^{-4}
Gelatin	1.00
ExM-3	0.25
Cpd-3	0.10
Cpd-4	0.05
Solv-2	0.05

Ninth Layer (Intermediate Layer)

Gelatin	0.50

Tenth Layer (Yellow Filter Layer)

Yellow colloidal silver	0.10
Gelatin	1.00
Cpd-1	0.05
Solv-1	0.03
Solv-2	0.07
Cpd-2	0.10

Eleventh Layer (Low Speed Blue Sensitive Layer)

Silver iodobromide emulsion (AgI=2.5 mol%, Regular crystal, twinned crystal mixture, Average grain size 0.7 μm)	0.55
ExS-5	1.00×10^{-3}
Gelatin	0.90
ExY-1	0.50
Solv-2	0.10

Twelfth Layer (High Speed Blue Sensitive Layer)

Tabular silver iodobromide emulsion (AgI=2.5 mol%, Grains with a diameter/thickness ratio of at least 5 accounted for 50% of the projected area of all the grains, Average thickness of grains 0.13 μm)	1.00
ExS-5	1.70×10^{-3}
Gelatin	2.00
ExY-1	1.00
Solv-2	0.20

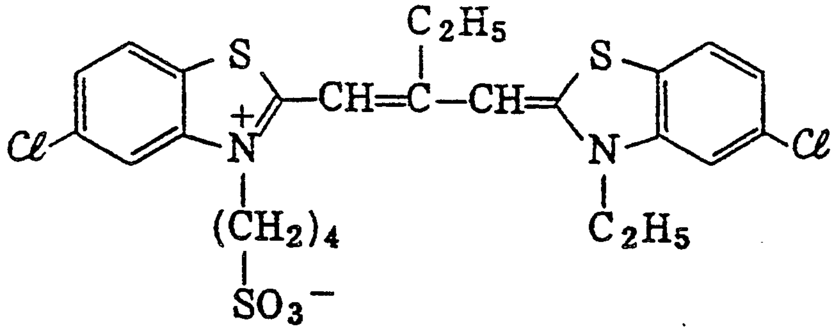
Thirteenth Layer (Ultraviolet Absorbing Layer)

Gelatin	1.50
UV-1	0.02
UV-2	0.04
UV-3	0.04
Cpd-5	0.30
Solv-1	0.30
Cpd-6	0.10

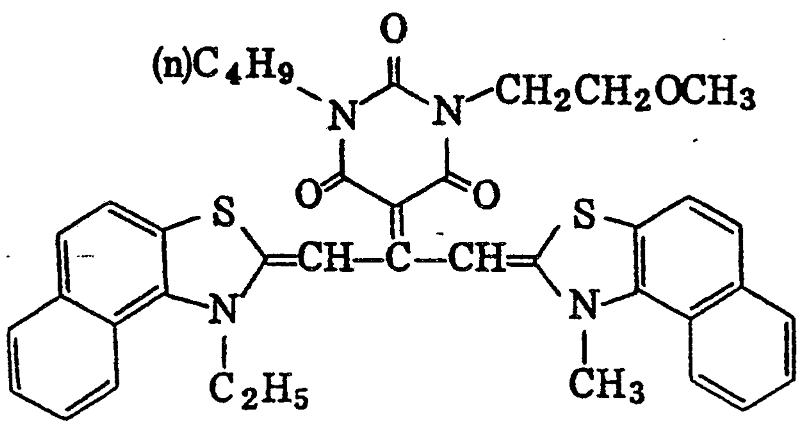
Fourteenth Layer (Protective Layer)

Fine grain silver iodobromide (AgI 1 mol%, Average grain size 0.05 μm)	0.10
Gelatin	2.00
H-1	0.30

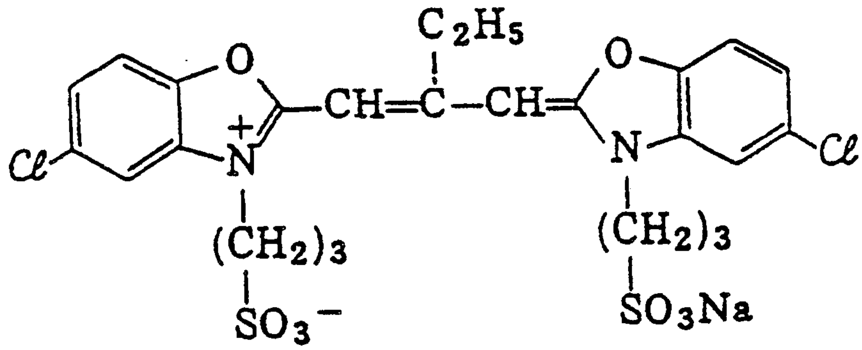
ExS-1


C2H5
S
S
CH=C-CH=
Cl
N
N
Cl
(CH2)4
C2H5
SO3

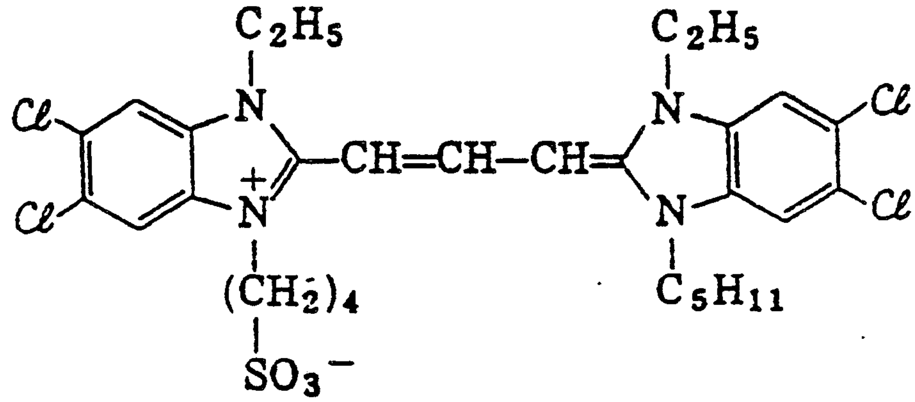
ExS-2


O
(n)C4H9
N
N
CH2CH2OCH3
O
O
S
S
=CH-C-CH=
N
N
C2H5
CH3

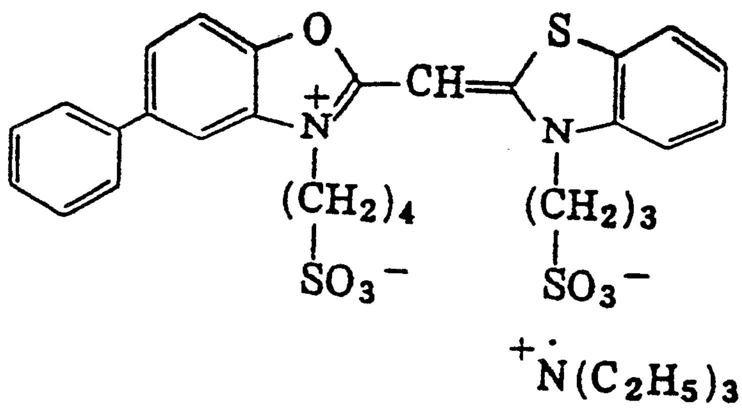
ExS-3



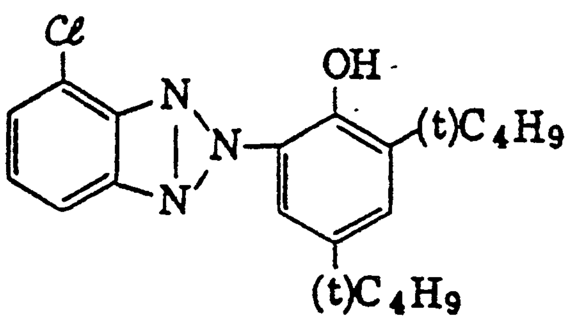
ExS-4



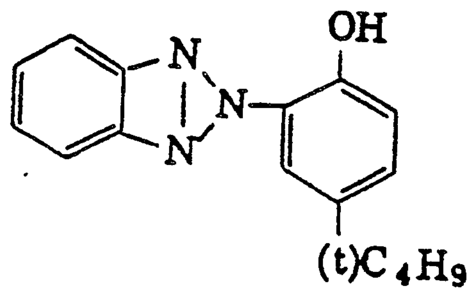
ExS-5



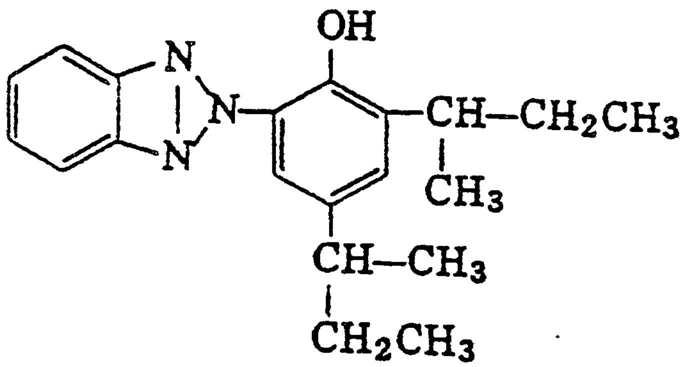
UV-1



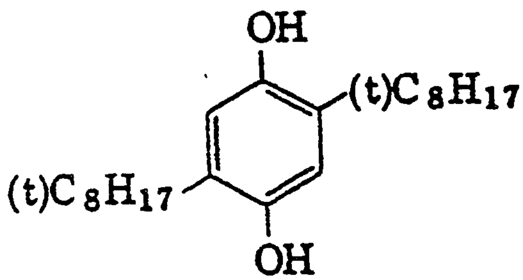
UV-2



UV-3



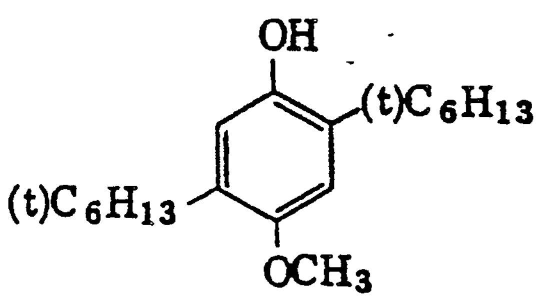
Cpd-1



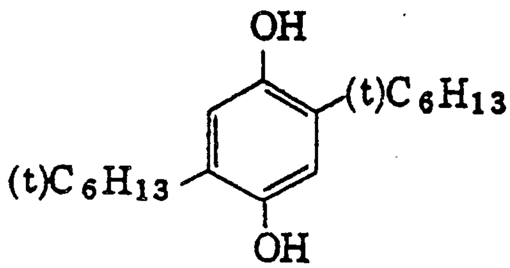
Cpd-2

Poly(ethyl acrylate)

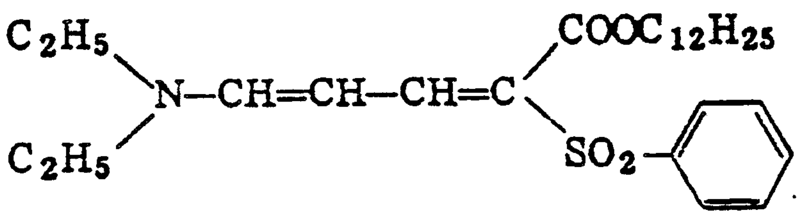
Cpd-3



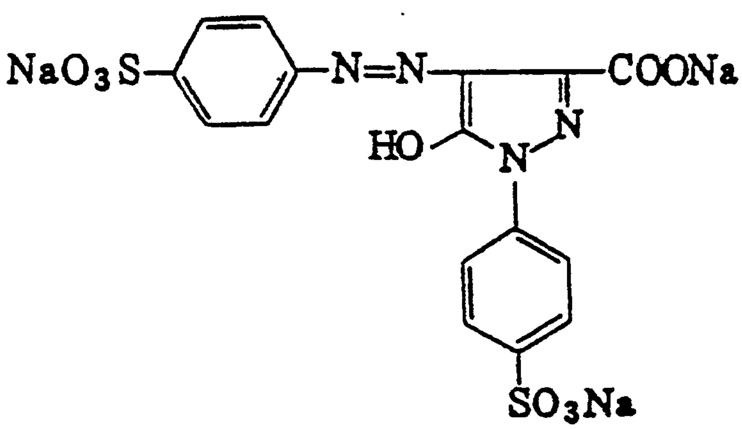
Cpd-4



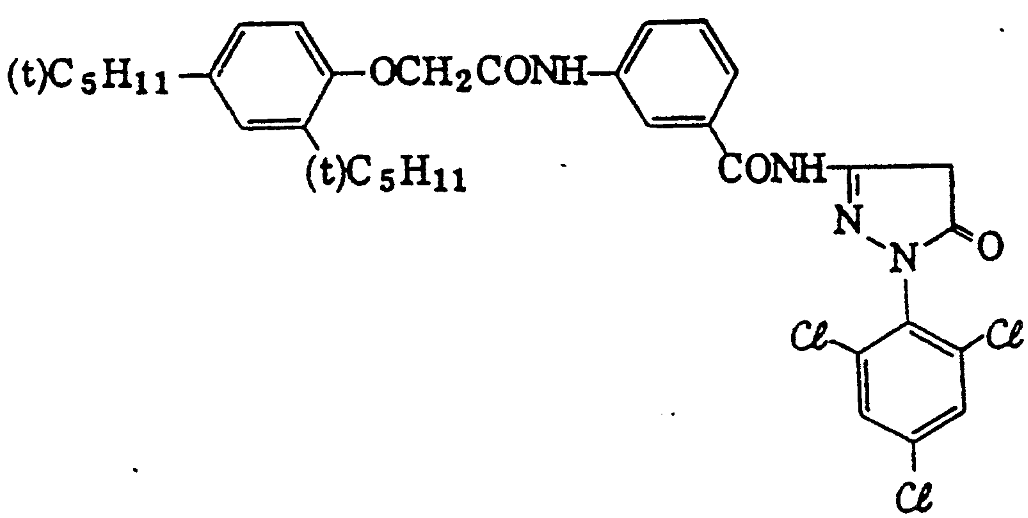
Cpd-5



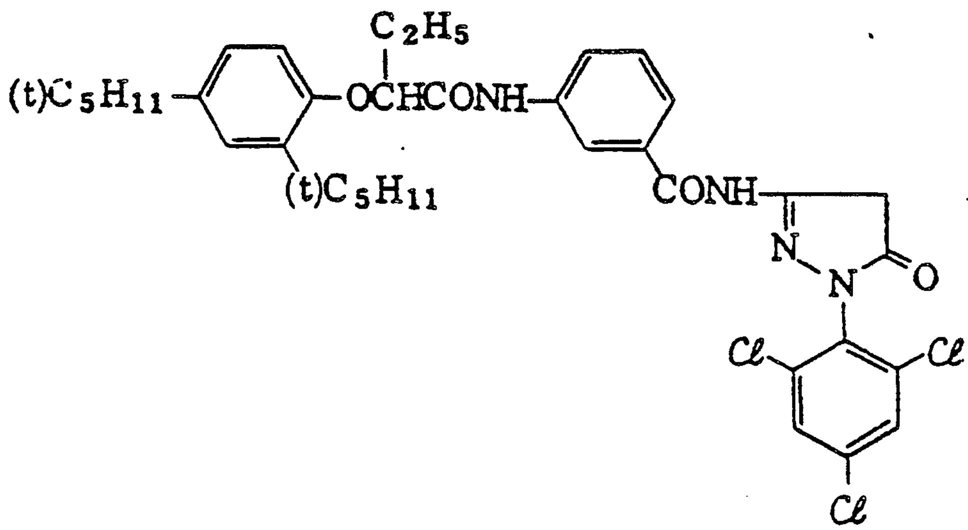
Cpd-6



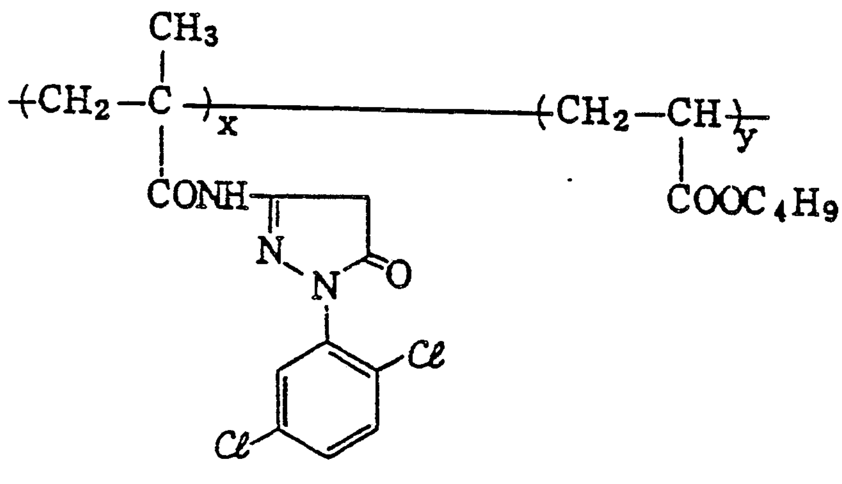
ExM-1



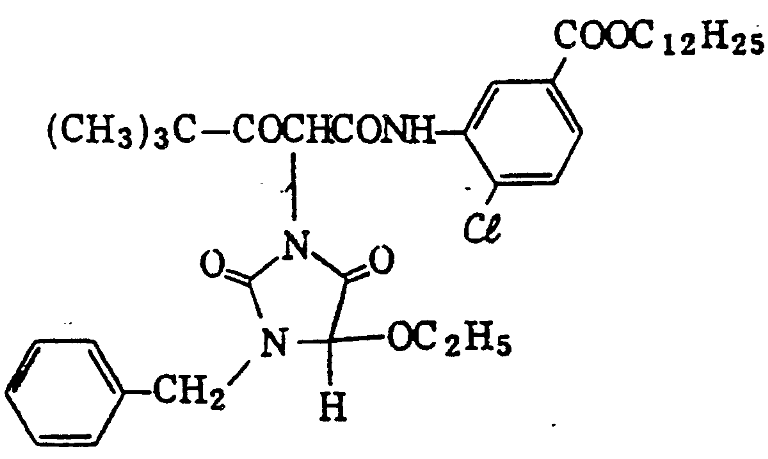
ExM-2



ExM-3



ExY-1



Solv-1:	Dibutyl phthalate
Solv-2:	Tricresyl phosphate
Solv-3:	Trinonyl phosphate
H-1:	1,2-bis(vinylsulfonylacetamido)ethane

Samples 102 to 110 were prepared by replacing the coupler (IV) of this invention added to the third, fourth and fifth layers of sample 101 with the same coated amounts (mol/square meter) of the couplers (V), (VI), (VII) and (III) of this invention and the comparative couplers (A), (B), (Q), (C) and (D).

The silver halide color photographic materials prepared in this way were processed in the way indicated below.

Processing Operation	Time	Temperature
First Development	6 minutes	38 °C
Water Wash	2 minutes	38 °C
Reversal	2 minutes	38 °C
Color Development	6 minutes	38 °C
Conditioning	2 minutes	38 °C
Bleaching	6 minutes	38 °C
Fixing	4 minutes	38 °C
Water Wash	4 minutes	38 °C
Stabilization	1 minute	25 °C

The compositions of the processing baths were as indicated below.

First Development Bath

Nitrilo-N,N,N-trimethylenephosphonic acid penta-sodium salt	2.0 g
Sodium sulfite	30 g
Hydroquinone monosulfonic acid, sodium salt	20 g
Potassium carbonate	33 g
1-Phenyl-4-methyl-4-hydroxymethyl-3 pyrazolidone	2.0 g
Potassium bromide	2.5 g
Potassium thiocyanate	1.2 g
Potassium iodide	2.0 g
Water	to make up to 1000 ml
pH	9.60

The pH was adjusted with hydrochloric acid or potassium hydroxide.

Reversal Bath

Nitrilo-N,N,N-trimethylenephosphonic acid penta-sodium salt	3.0 g
Stannous chloride dihydrate	1.0 g
p-Aminophenol	0.1 g
Sodium hydroxide	8 g
Glacial acetic acid	15 ml
Water	to make up to 1000 ml
pH	6.00

The pH was adjusted with hydrochloric acid or sodium hydroxide.

Color Development bath

Nitrilo-N,N,N-trimethylenephosphonic acid penta-sodium salt	2.0 g
Sodium sulfite	7.0 g
Trisodium phosphate dodecahydrate	36 g
Potassium bromide	1.0 g
Potassium iodide	90 mg
Sodium hydroxide	3.0 g
Citrazinic acid	1.5 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	11 g
3,6-Dithiaoctane-1,8-diol	1.0 g
Water	to make up to 1000 ml
pH	11.80

The pH was adjusted with hydrochloric acid or potassium hydroxide.

Conditioner Bath

Ethylenediamine tetra-acetic acid, disodium salt, dihydrate	8.0 g
Sodium sulfite	12 g
1-Thioglycerine	0.4 ml
Water	to make up to 1000 ml
pH	6.20

The pH was adjusted using hydrochloric acid or potassium hydroxide.

Bleach Bath

Ethylenediamine tetra-acetic acid, disodium salt, dihydrate	2.0 g
Ethylenediamine tetra-acetic acid, Fe(III), ammonium salt, dihydrate	120 g
Potassium bromide	100 g
Ammonium nitrate	10 g
Water	to make up to 1000 ml
pH	5.70

The pH was adjusted using hydrochloric acid or potassium hydroxide.

Fixing Bath

Ammonium thiosulfate	80 g
Sodium sulfite	5.0 g
Sodium bisulfite	5.0 g
Water	to make up to 1000 ml
pH	6.60

The pH was adjusted using hydrochloric acid or potassium hydroxide.

Stabilizer Bath

Formalin (37%)	5.0 ml
Polyoxyethylene p-monononylphenyl ether (average degree of polymerization 10)	0.5 ml
Water	to make up to 1000 ml
pH	not adjusted

The cyan densities of the cyan images and the relative speeds of the processed samples were measured.

The results obtained were as shown in Table 2.

TABLE 2

Sample	coupler (Coupler Monomer)		Chain Transfer Agent (Chain Transfer Constant) (wt%)		Coupler Monomer Content of Polymer	No. Ave. Molecular Weight	Cyan colored Image		Remarks
							D_{max}*	Rel. Speed**	
101	IV	(14)	$C_{12}H_{25}SH$	2.9	49.8	2800	3.15	0.10	This Invention
102	V	(14)	***	1.1	50.7	2300	3.25	0.11	"
103	VI	(14)	$C_{18}H_{37}SH$	2.3	73.8	1700	2.95	0.10	"
104	VII	(14)	$C_{12}H_{25}SH$	2.9	89.5	2000	2.90	0.09	"
105	III	(2)	$C_{12}H_{25}SH$	2.6	50.8	2100	3.10	0.10	"
106	(A)	(14)	-	-	50.2	41000	1.90	0.00	Comparative Example
107	(B)	(14)	-	-	48.7	3700	3.00	0.00	"
108	(Q)	(14)	2-hexadecanol	about 1×10^{-3}	49.5	29000	2.00	0.01	"
109	(C)	(14)	-	-	74.6	18000	0.95	-0.10	"
110	(D)	(14)	-	-	73.9	3200	2.05	-0.08	"

*: D_{max}-Maximum color density

**: Relative Speed-Represented by the relative value of the reciprocal of the exposure required to provide D=0.5, taking the value for sample 107 to be 0.00

***: $C_2H_5-CH(CH_3)-(CH_2)_4-OC(=O)CH_2SH$

It is clear from Table 2 that the samples which contained the telomeric couplers of this invention had a high color forming ability irrespective of the coupler unit content, and that they had markedly higher speeds than the comparative couplers (conventional polymeric couplers and couplers obtained using chain transfer agents of which the chain transfer constant was outside the range from 0.1 to 20).

EXAMPLE 2

Sample 201, a multi-layer color photosensitive material consisting of layers of which the compositions are indicated below was prepared on an undercoated cellulose triacetate film suppcrt.

Composition of the Photosensitive Layer

The amounts coated are expressed in units of grams of silver per square meter in the case of the silver halides and colloidal silver, in units of grams per square meter in the case of couplers, additives and gelatin, and in units of mols per mol of silver halide in the same layer in the case of the sensitizing dyes.

First Layer (Anti-halation Layer)

Black colloidal silver	0.2
Gelatin	1.3
ExM-9	0.06
UV-1	0.03
UV-2	0.06
UV-3	0.06
Solv-1	0.15
Solv-2	0.15
Solv-3	0.05

Second Layer (Intermediate Layer)

Gelatin	1.0
UV-1	0.03
ExC-4	0.02
ExF-1	0.004
Solv-1	0.1
Solv-2	0.1

Third Layer (Low Speed Red Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 4 mol%, Uniform AgI type, Corresponding sphere diameter 0.5 μ, Variation coefficient of corresponding sphere diameter 20%, Tabular grains, Diameter/thickness ratio 3.0)	Coated silver weight 1.2
Silver iodobromide emulsion (AgI 3 mol%, Uniform AgI type, Corresponding sphere diameter 0.3 μ, Variation coefficient of corresponding sphere diameter 15%, Tabular grains, Diameter/thickness ratio 1.0)	Coated silver weight 0.6
Gelatin	1.0
ExS-1	4×10^{-4}
ExS-2	5×10^{-5}
ExC-1	0.05
ExC-2	0.50
ExC-3	0.03
ExC-4	0.12
ExC-5	0.01
ExC-8	0.03

Fourth Layer (High Speed Red Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 6 mol%, Core/shell ratio 1:1, high internal AgI type, Corresponding sphere diameter 0.7 μm, Variation coefficient of corresponding sphere diameter 15%, Tabular grains, Diameter/thickness ratio 5.0)	Coated silver weight 0.7
Gelatin	1.0
ExS-1	3×10^{-4}
ExS-2	2.3×10^{-5}
ExC-6	0.11
ExC-7	0.05
ExC-4	0.05
Solv-1	0.05
Solv-3	0.05

Fifth Layer (Intermediate Layer)

Gelatin	0.5
Cpd-1	0.1
Solv-1	0.05

Sixth Layer (Low Speed Green Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 4 mol%, Core/shell ratio 1:1, high internal AgI type, Corresponding sphere diameter 0.5 μm, Variation coefficient of corresponding sphere diameter 15%, Tabular grains, Diameter/thickness ratio 3.0)	Coated silver weight 0.35

Silver iodobromide emulsion (AgI 3 mol%, Uniform AgI type, Corresponding sphere diameter 0.3 μm, Variation coefficient of corresponding sphere diameter 25%, Spherical grains, Diameter/thickness ratio 1.0)	Coated silver weight 0.20
Gelatin	1.0
ExS-3	5×10^{-4}
ExS-4	3×10^{-4}
ExS-5	1×10^{-4}
Coupler (XI) of this invention	0.4
ExM-9	0.07
ExM-10	0.02
ExY-11	0.03
Solv-1	0.3
Solv-4	0.05

Seventh Layer (High Speed Green Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 4 mol%, Core/shell ratio 1:1, high internal AgI type, Corresponding sphere diameter 0.7 μm, Variation coefficient of corresponding sphere diameter 20%, Tabular grains, Diameter/thickness ratio 5.0)	Coated silver weight 0.8
Gelatin	0.5
ExS-3	5×10^{-4}
ExS-4	3×10^{-4}
ExS-5	1×10^{-4}
Coupler (XI) of this invention	0.1
ExM-9	0.02
ExY-11	0.03
ExC-2	0.03

ExM-14	0.04
Solv-1	0.2
Solv-4	0.01

Eighth Layer (Intermediate Layer)

Gelatin	0.5
Cpd-1	0.05
Solv-1	0.02

Ninth Layer (Lamination Effect Donor Layer for the Red Sensitive Layer)

Silver iodobromide emulsion (AgI 2 mol%, Core/shell ratio 2:1, high internal AgI type, Corresponding sphere diameter 1.0 µm, Variation coefficient of corresponding sphere diameter 15%, Tabular grains, Diameter/thickness ratio 6.0)	Coated silver weight 0.35
Silver iodobromide emulsion (AgI 2 mol%, Core/shell ratio 1:1, high internal AgI type, Corresponding sphere diameter 0.4 µm, Variation coefficient of corresponding sphere diameter 20%, Tabular grains, Diameter/thickness ratio 6.0)	Coated silver weight 0.20
Gelatin	0.5
ExS-3	8×10^{-4}
ExY-13	0.11
ExM-12	0.03
ExM-14	0.10
Solv-1	0.20

Tenth Layer (Yellow Filter Layer)

Yellow colloidal silver	0.05
Gelatin	0.5
Cpd-2	0.13
Solv-1	0.13
Cpd-1	0.10

Eleventh Layer (Low Speed Blue Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 4.5 mol%, Uniform AgI type, Corresponding sphere diameter 0.7 µm, Variation coefficient of corresponding sphere diameter 15%, Tabular grains, Diameter/thickness ratio 7.0)	Coated silver weight 0.3
Silver iodobromide emulsion (AgI 3 mol%, Uniform AgI type, Corresponding sphere diameter 0.3 µm, Variation coefficient of corresponding sphere diameter 25%, Tabular grains, Diameter/thickness ratio 7.0)	Coated silver weight 0.15
Gelatin	1.6
ExS-6	2×10^{-4}
ExC-16	0.05
ExC-2	0.10
ExC-3	0.02
ExY-13	0.07
ExY-15	1.0
Solv-1	0.20

Twelfth Layer (High Speed Blue Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 10 mol%, high internal AgI type, Corresponding sphere diameter 1.0 µm, Variation coefficient of corresponding sphere diameter 25%, Tabular grains, Diameter/thickness ratio 2.0)	Coated silver weight 0.5
Gelatin	0.5
ExS-6	1×10^{-4}
ExY-15	0.20
ExY-13	0.01
Solv-1	0.10

Thirteenth Layer (First Protective Layer)

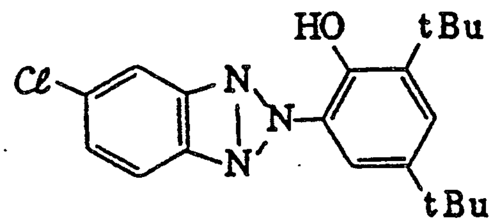
Gelatin	0.8
UV-4	0.1
UV-5	0.15
Solv-1	0.01
Solv-2	0.01

Fourteenth Layer (Second Protective Layer)

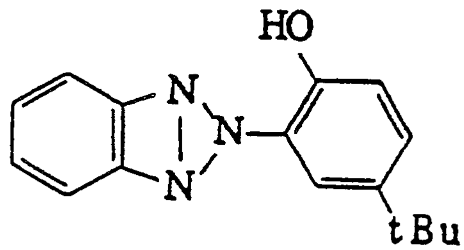
Fine grain silver bromide emulsion (AgI 2 mol%, Uniform AgI type, Corresponding sphere diameter 0.07 µm)	0.5
Gelatin	0.45
Poly(methyl methacrylate) grains Diameter 1.5 µ	0.2
H-1	0.4
Cpd-5	0.5
Cpd-6	0.5
Cpd-8	0.2

The emulsion stabilizer Cpd-3 (0.04 gram per square meter) and the surfactant Cpd-4 (0.02 gram per square meter) as coating promoter were added to each layer as well as the components mentioned above.

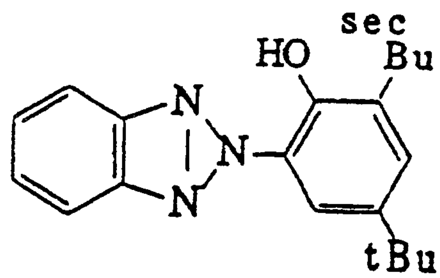
UV-1



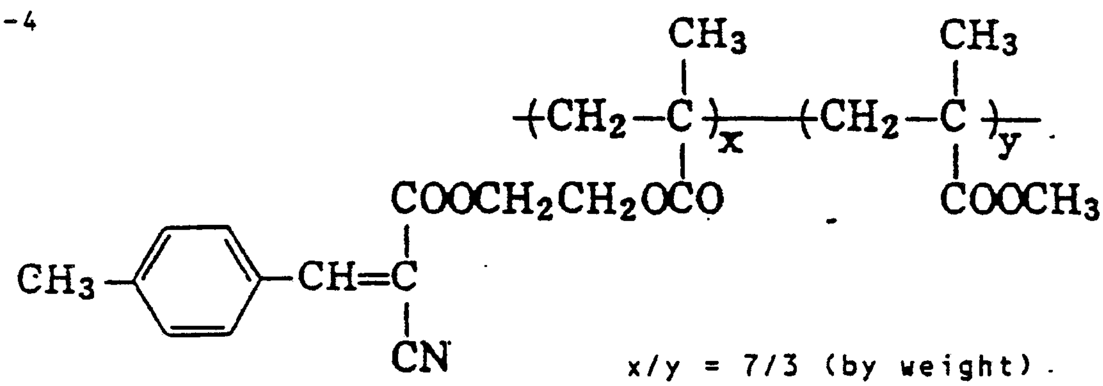
UV-2



UV-3

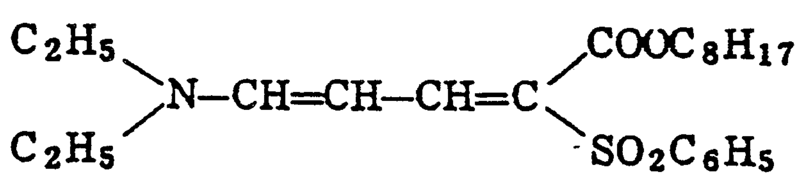


UV-4



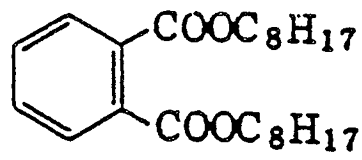
x/y = 7/3 (by weight)

UV-5

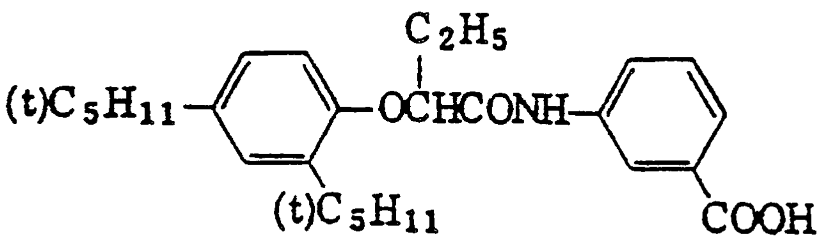


Solv-1 Tricresyl phosphate
Solv-2 Dibutylphthalate

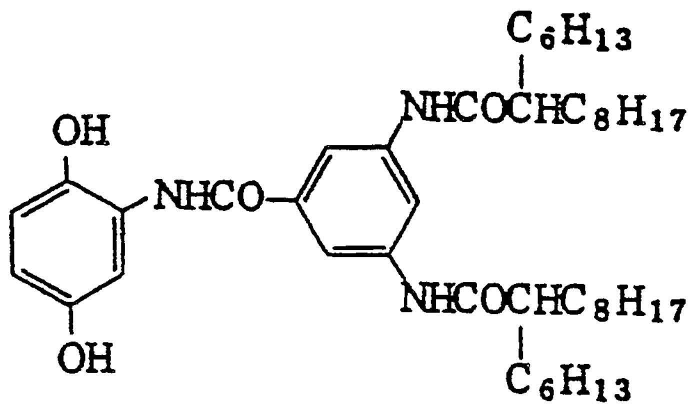
Solve-3



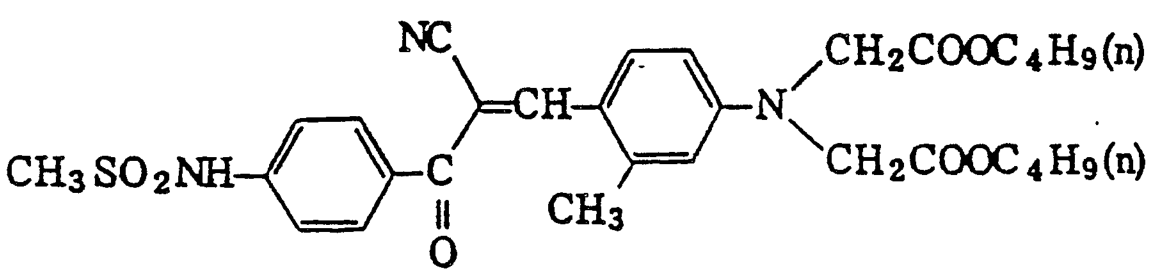
Solv-4



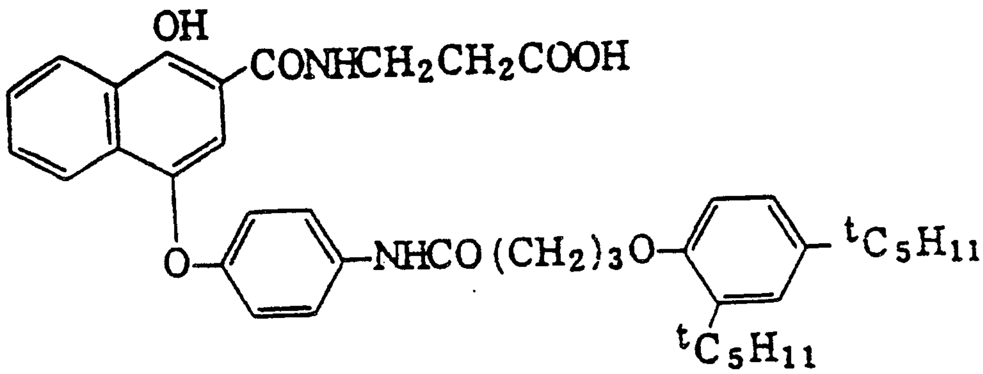
Cpd-1



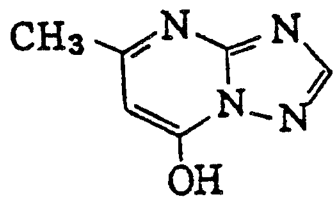
Cpd-2



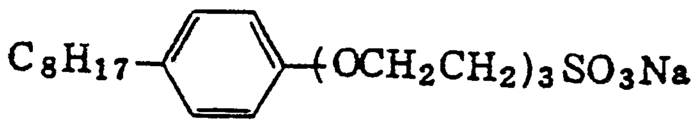
Cpd-7



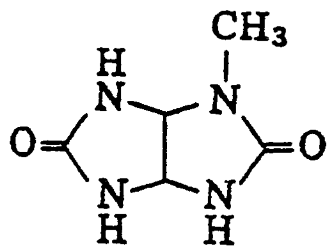
Cpd-3



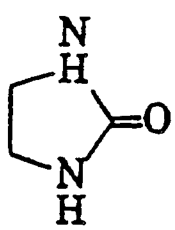
Cpd-4



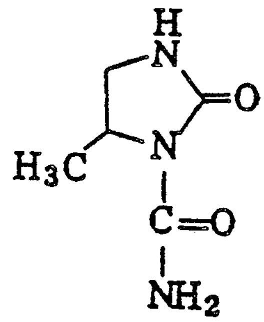
Cpd-5



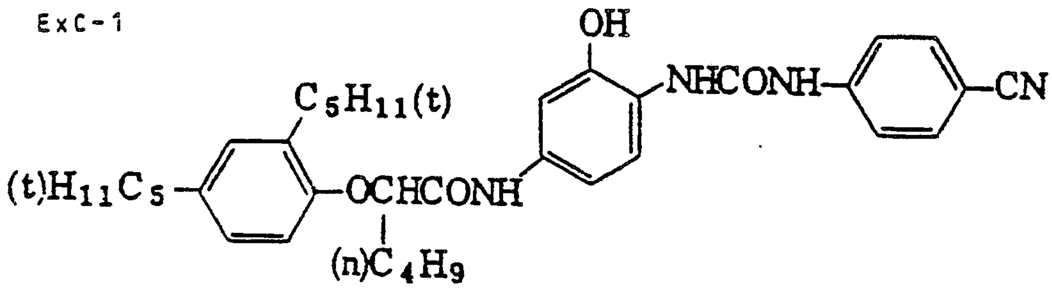
Cpd-6



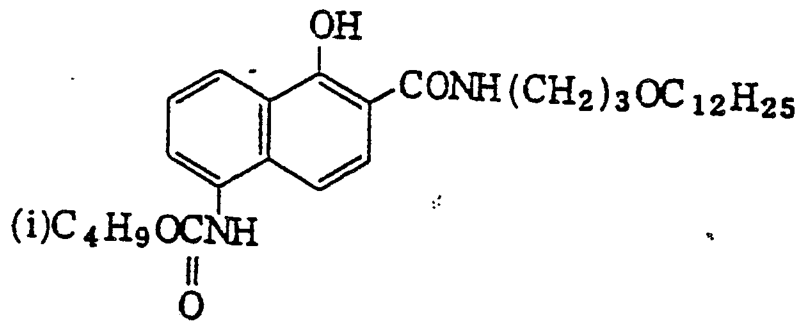
Cpd-8



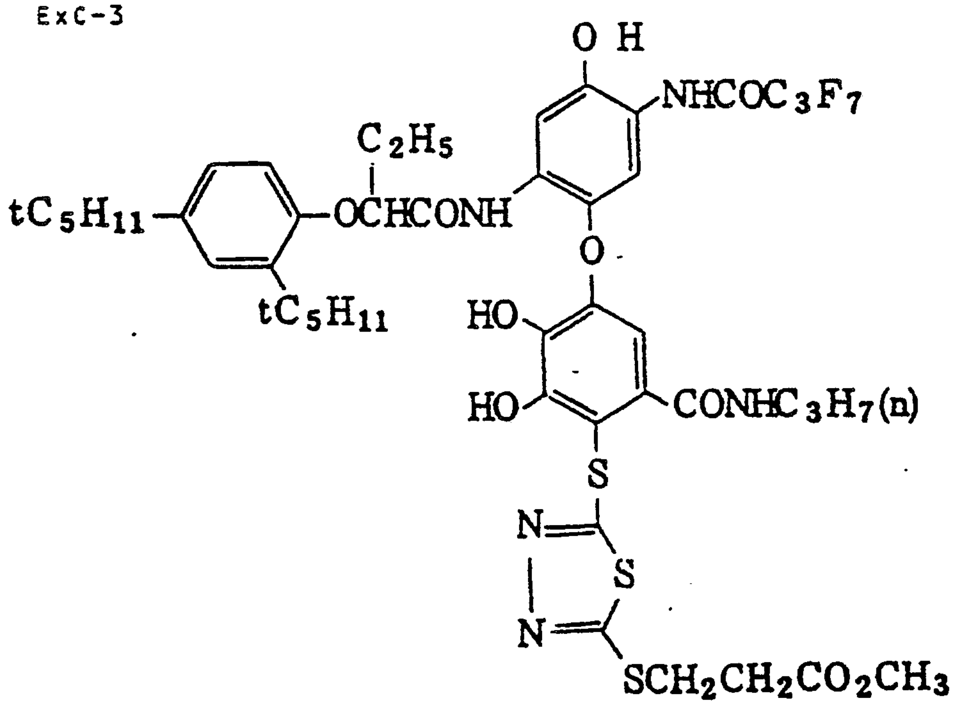
ExC-1



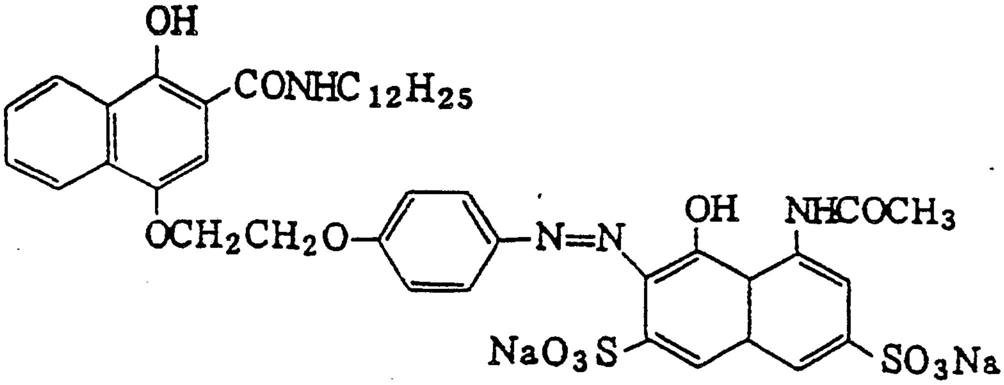
ExC-2



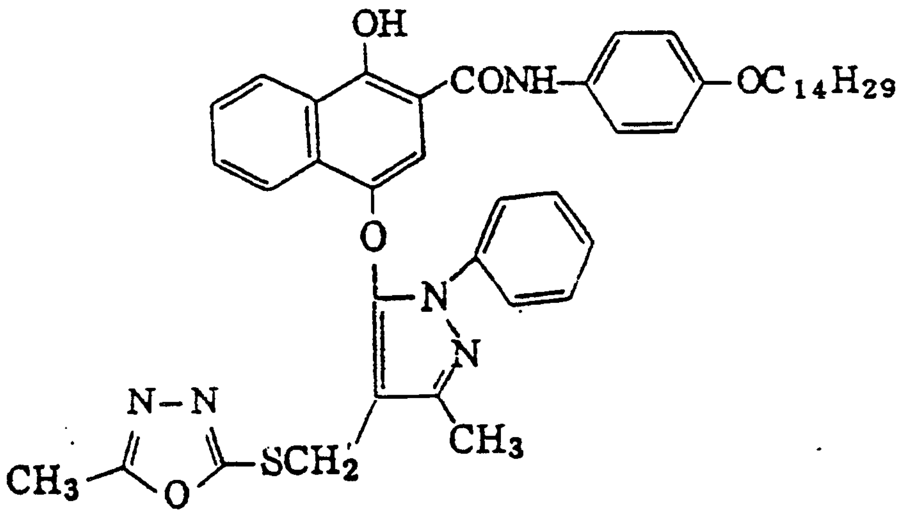
ExC-3



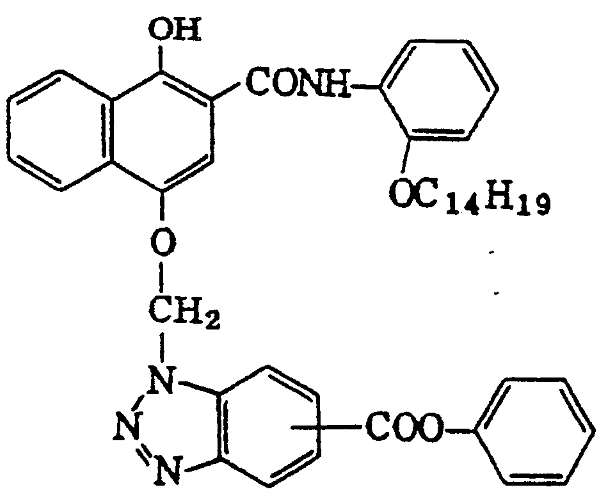
ExC-4



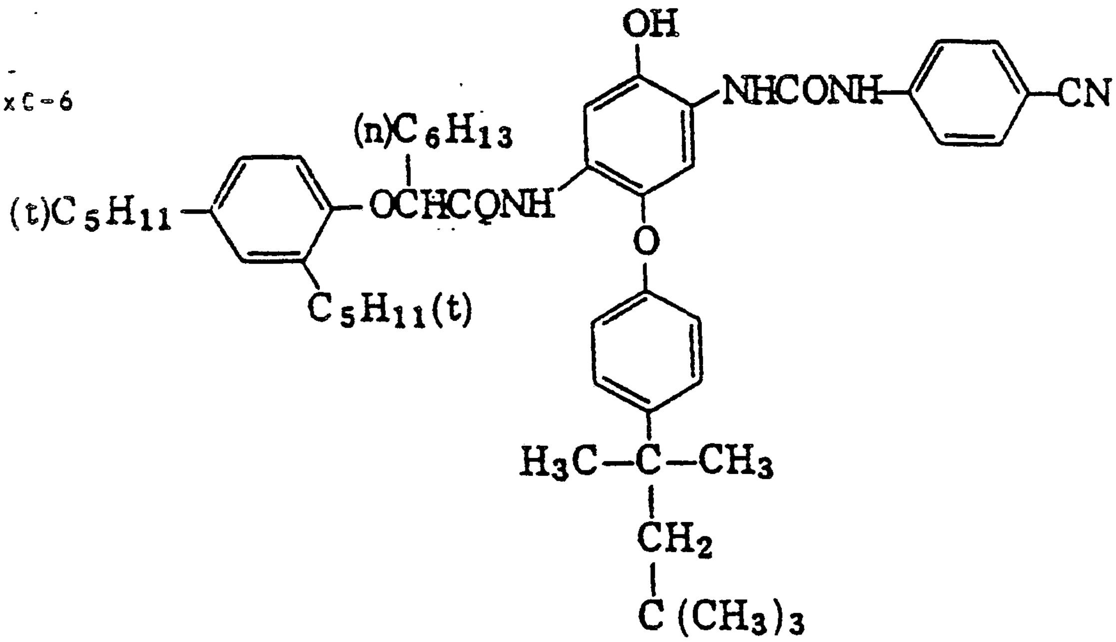
ExC-8



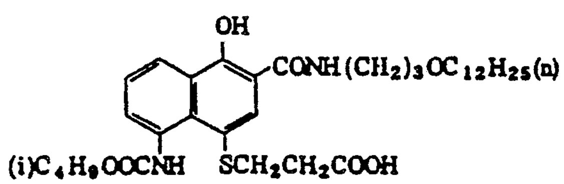
ExC-5



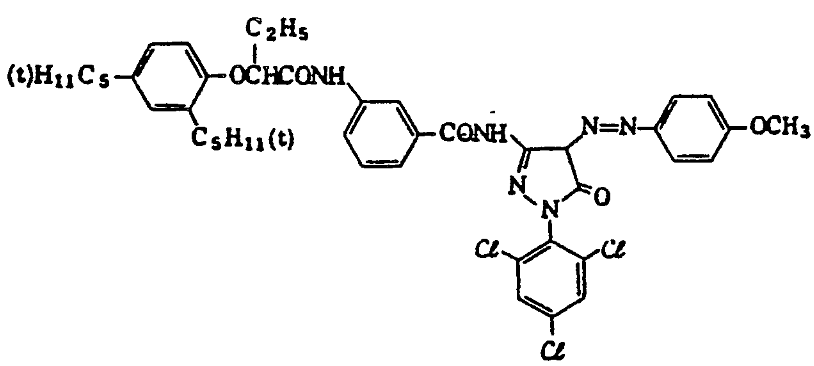
ExC-6



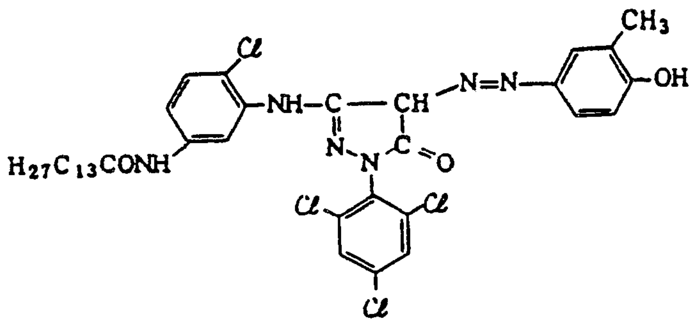
ExC-7



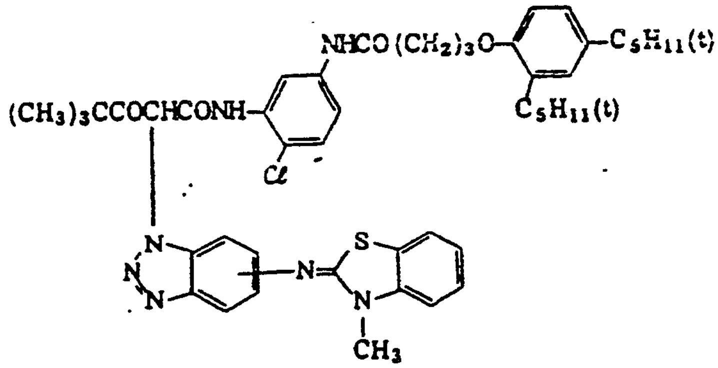
Ex M-9



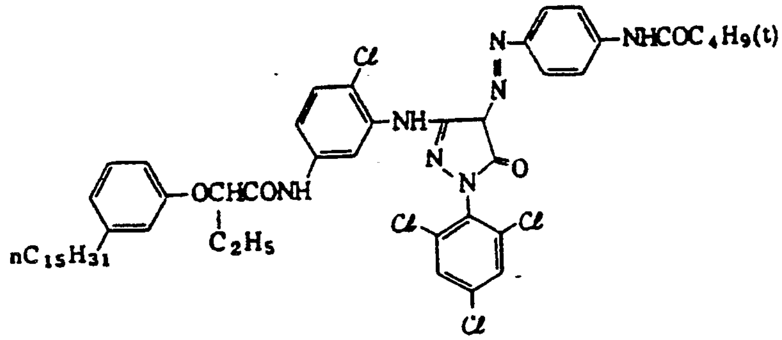
ExM-10



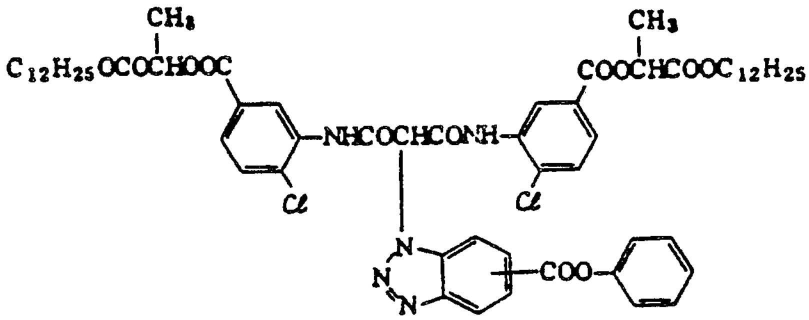
Ex-Y-11



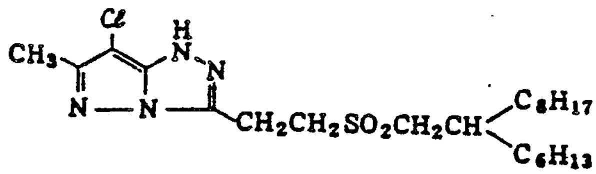
ExY-12



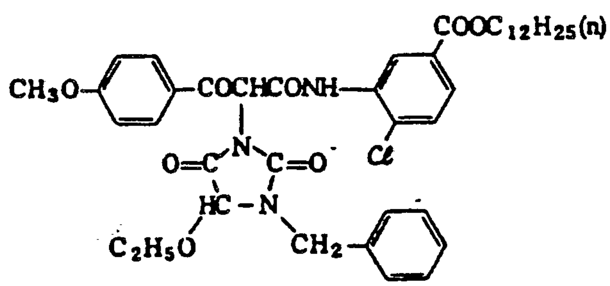
ExY-13



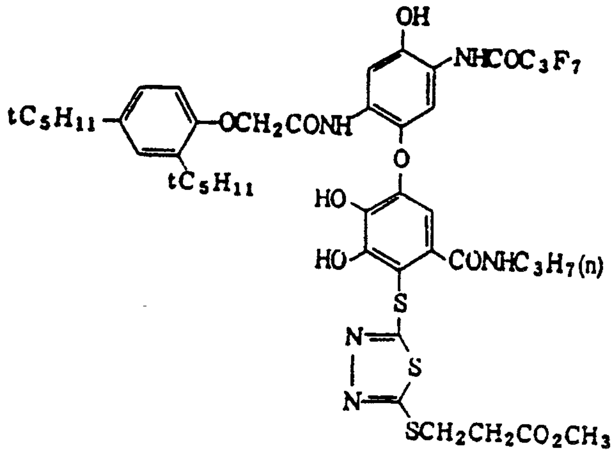
ExM-14



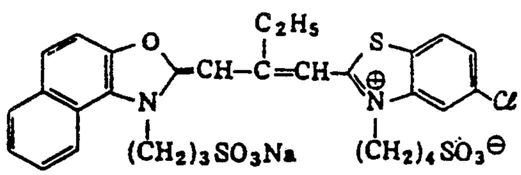
ExM-15



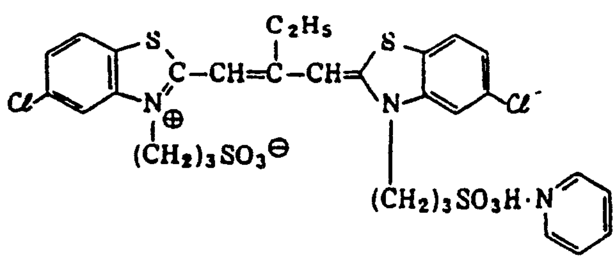
ExM-16



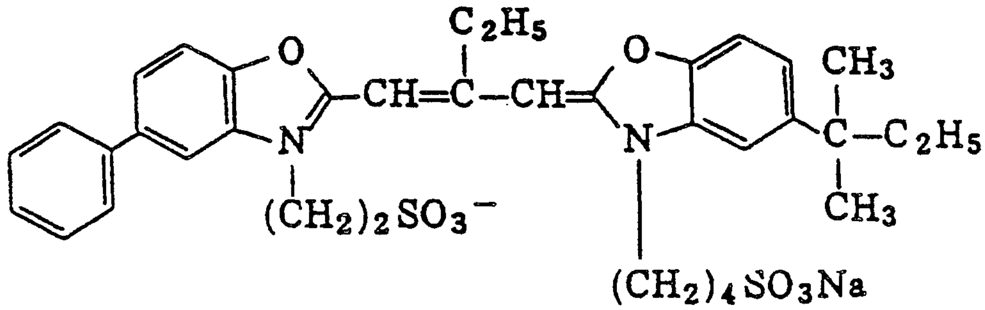
ExS-1



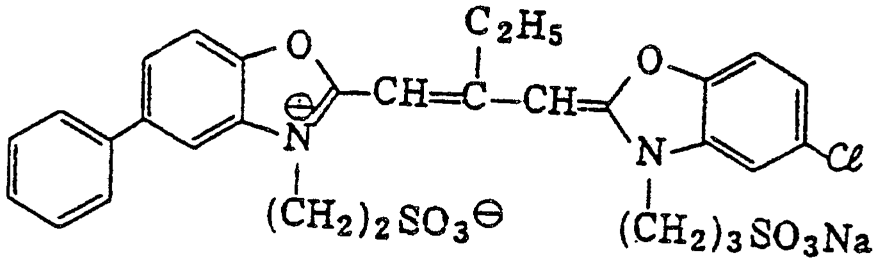
ExS-2



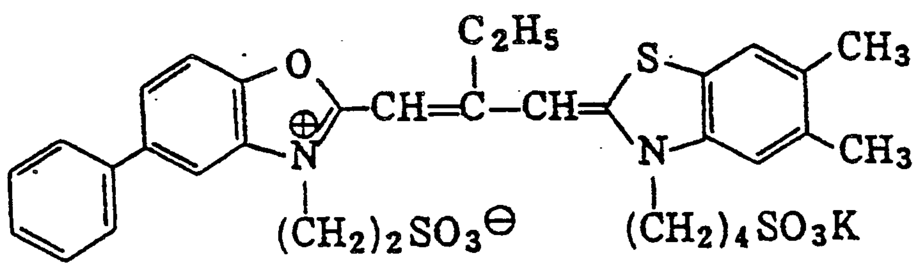
ExS-3



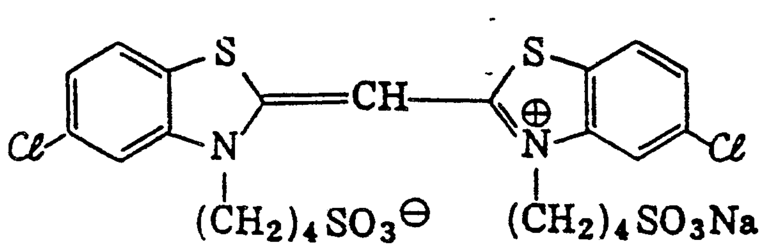
ExS-4



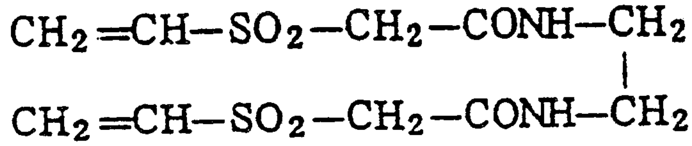
ExS-5



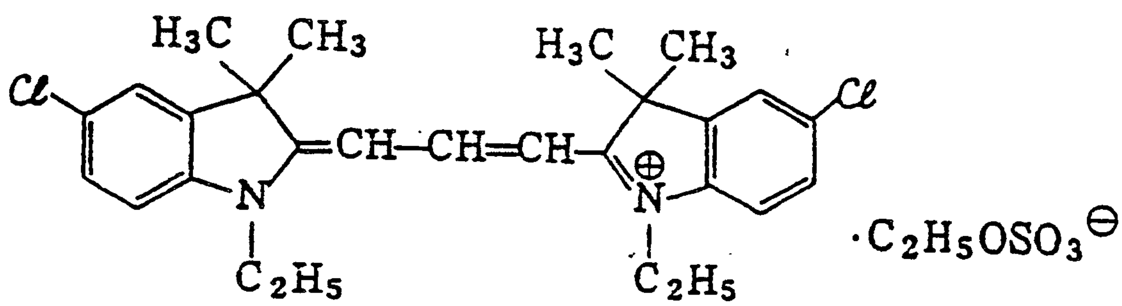
ExS-6



H-1



ExF-1



Samples 202 to 207 were prepared in the same way as sample 201 except that the coupler (XI) of the invention added to the sixth and seventh layers of sample 201 was replaced with coupler (XII) of this invention and comparative couplers (E), (G), (R), (F) and (H) with equal coupler units, as shown in Table 3.

The silver halide color photographic materials prepared in this was were processed in the way indicated below after exposure through a continuous wedge.

Processing Operation		
Process	Processing Time	Processing temp.
Color Development	3 min. 15 sec.	38 °C
Bleaching	6 min. 30 sec.	38 °C
Water Wash	2 min. 10 sec.	24 °C
Fixing	4 min. 20 sec.	38 °C
Water Wash (1)	1 min. 05 sec.	24 °C
Water Wash (2)	2 min. 10 sec.	24 °C
Stabilization	1 min. 05 sec.	38 °C
Drying	4 min. 20 sec.	55 °C

The compositions of the processing baths are indicated below.

Color Development Bath

	(Units: grams)
Diethylenetriamine penta-acetic acid	1.0
1-hydroxyethylidene-1,1-diphosphonic acid	3.0
Sodium sulfite	4.0
Potassium carbonate	30.0
Potassium bromide	1.4
Potassium iodide	1.5 mg
Hydroxylamine sulfate	2.4
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5
Water	to make up to 1.0 ℓ
pH	10.05

Bleach Bath

	(Units: grams)
Ethylenediamine tetra-acetic acid, ferric sodium salt trihydrate	100.0
Ethylenediamine tetra-acetic acid, disodium salt	10.0
Ammonium bromide	140.0
Ammonium nitrate	30.0
Aqueous ammonia (27%)	6.5 ml
Water	to make up to 1.0 ℓ
pH	6.0

Fixing Bath

	(Units: grams)
Ethylenediamine tetra-acetic acid, disodium salt	0.5
Sodium sulfite	7.0
Sodium bisulfite	5.0
Aqueous ammonium thiosulfate solution (70%)	170.0 ml
Water	to make up to 1.0 ℓ
pH	6.7

Stabilizing Bath

	(Units: grams)
Formalin (37%)	2.0 ml
Polyoxyethylene-p-monononylphenyl ether (average degree of polymerization 10)	0.3
Ethylenediamine tetra-acetic acid, disodium salt	0.05
Water	to make up to 1.0 ℓ
pH	5.0 - 8.0

The densities of the magenta images and the speeds of the processed samples were measured. The results obtained were shown in Table 3.

TABLE 3

Sample	Coupler	Chain Transfer Agent (Chain Transfer Constant)		Coupler Monomer Content of Polymer (wt%)	No. Ave. Molecular Weight	Photographic Characteristics			Remarks
						Rel. Speed[1]	Gamma[2]	Color Density[3]	
201	(XI)	$C_{18}H_{37}SH$	1.8	50.3	1700	0.08	0.71	2.20	This Invention
202	(XII)	$C_{12}H_{25}SH$	3.2	70.5	3000	0.08	0.68	2.15	"
203	(E)	-	-	50.8	21000	0.00	0.64	2.05	Comparative Example
204	(G)	-	-	48.5	3600	-0.04	0.64	2.10	"
205	(R)	2-hexadecanol	About 1×10^{-3}	51.4	15000	0.00	0.65	2.10	"
206	(F)	-	-	75.3	13000	-0.05	0.61	1.80	"
207	(H)	-	-	73.6	3800	-0.08	0.62	1.92	"

1: Relative value of log of the reciprocal of the exposure required to give a density of fog + 0.2 when the value for sample 201 is 0.00.
2: Gradient of the line joining the points of density fog + 0.2 and fog + 1.0.
3: Magenta density at 1 CMS.

It is clear from the results shown in Table 3 that the telomeric couplers of this invention provide a harder gradation at high speed and a higher color density than the comparative couplers (conventional polymeric couplers and couplers obtained using a chain transfer agent of which the chain transfer constant is outside the range from 0.1 to 20).

EXAMPLE 3

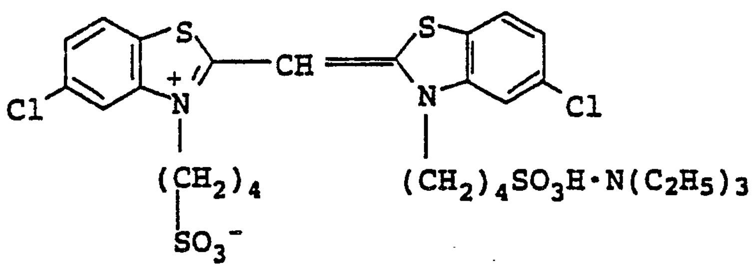
A multi-layer color printing paper of which the structure is indicated below was prepared on a paper support which had been laminated on both sides with polyethylene.

Preparation of the First Layer Coating Liquid

Ethyl acetate (27.2 cc) and 7.7 cc of solvent (Soly-2) were added to 19.1 grams of yellow coupler EXY) and 4.40 grams of anti-color fading agent (Cpd-1) to form a solution, and this solution was emulsified and dispersed in 185 cc of 10% aqueous gelatin solution which contained 8 cc of 10% sodium dodecylbenzenesulfonate. Moreover, a silver chlorobromide emulsion (silver bromide content 80.8 mol%, containing 70 grams of silver per kilogram) to which the blue sensitizing dye indicated below hade been added at a rate of 5.0×10-4 per mol of silver was also prepared. The above mentioned emulsified dispersion and the above mentioned emulsion were mixed together and dissolved to provide the first layer coating liquid of which the composition is indicated below. The coating layers for the second to the seventh layers were prepared in the same way as the first layer coating liquid. 1-Oxy-3,5-dichloro-s-triazine, sodium salt, was used as a gelatin hardening agent in each layer.

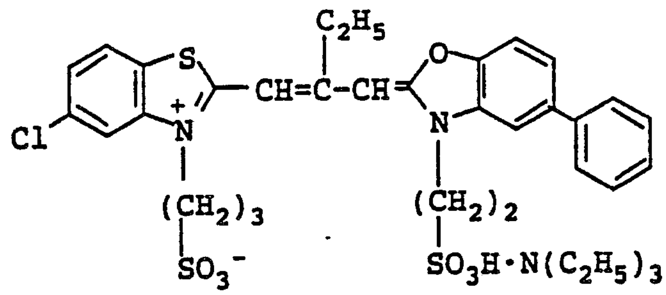
Furthermore, the compounds indicated below were used as spectral sensitizing dyes in each layer.

Blue Sensitive Emulsion Layer

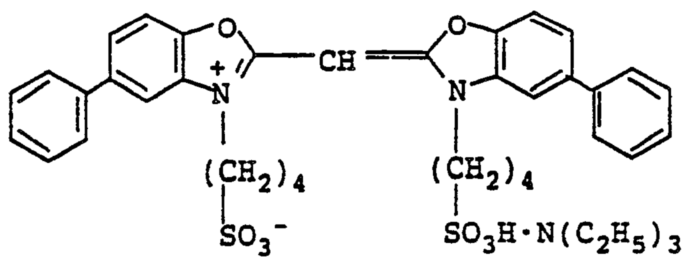


(5.0×10^{-4} mol per mol of silver halide)

Green Sensitive Emulsion Layer

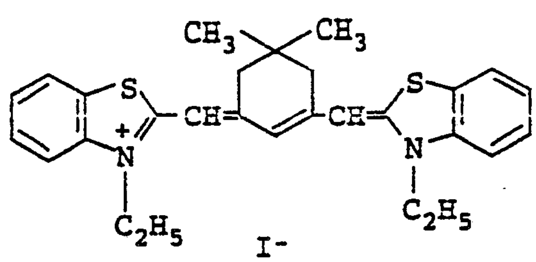


(4.0×10^{-4} mol per mol of silver halide)
and



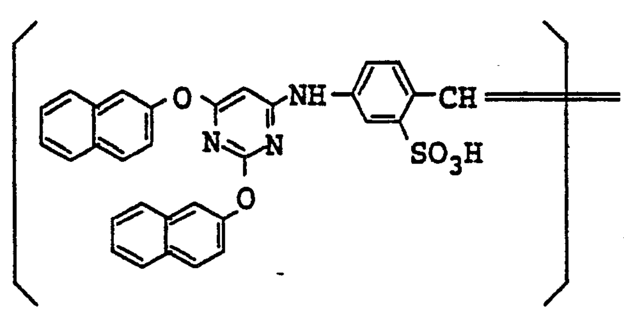
(7.0×10^{-5} mol per mol of silver halide)

Red Sensitive Emulsion Layer



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

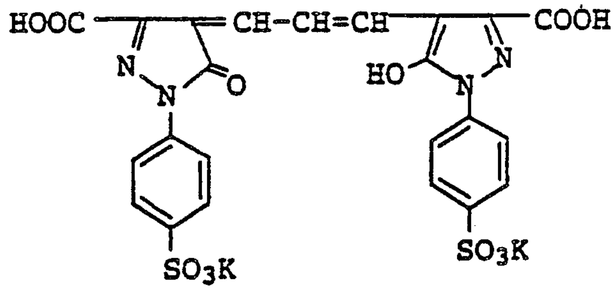
The compound indicated below was added at a rate of 2.6×10^{-3} mol per mol of silver halide to the red sensitive emulsion layer.



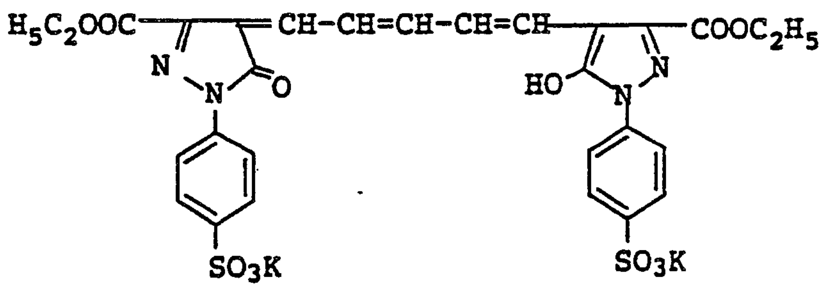
Moreover, 1-(5-methylureidophenyl)-5-mercaptotetrazole was added to the blue sensitive, green sensitive and red sensitive emulsion layers at the rates of 4.0×10^{-6} mol, 3.0×10^{-5} mol and 1.0×10^{-5} mol, per mol of silver halide, respectively.

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

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



and



Layer Structure

The composition of each layer is indicated below. The numerical values indicate the coated weights (grams per square meter) or, in the case of the silver halide emulsions, the coated weights calculated as silver.

Support

Paper support which was laminated with polyethylene on both sides [White pigment (TiO_2) and a blue dye (ultramarine) were included in the polyethylene on the first layer side].

First Layer (Blue Sensitive Layer)

Silver halide emulsion (Br: 80%)	0.35
Gelatin	1.83
Yellow coupler (EXY)	0.83
Colored image stabilizer (Cpd-1)	0.19
Solvent (Solv-1)	0.35

Second Layer (Anti-color Mixing Layer)

Gelatin	0.99
Anti-color mixing agent (Cpd-2)	0.08

Third Layer (Green Sensitive Layer)

Silver Halide emulsion (Br: 80 mol%)	0.19
Gelatin	1.23
Magenta coupler (E×M)	0.28
Colored image stabilizer (Cpd-3)	0.08
Colored image stabilizer (Cpd-9)	0.06
Anti-staining agent (Cpd-10)	0.15
Solvent (Solv-4)	0.27

Fourth Layer (Ultraviolet Absorbing Layer)

Gelatin	1.58
Ultraviolet Absorber (UV-1)	0.07
(UV-2)	0.30
(UV-3)	0.25
Anti-color mixing agent (Cpd-6)	0.05
Solvent (Solv-2)	0.24

Fifth Layer (Red Sensitive Layer)

Silver halide emulsion (Br: 70%)	0.23
Gelatin	1.34
Cyan coupler of this invention (I)	0.38
Colored image stabilizer (Cpd-7)	0.17
Solvent (Solv-1)	0.23

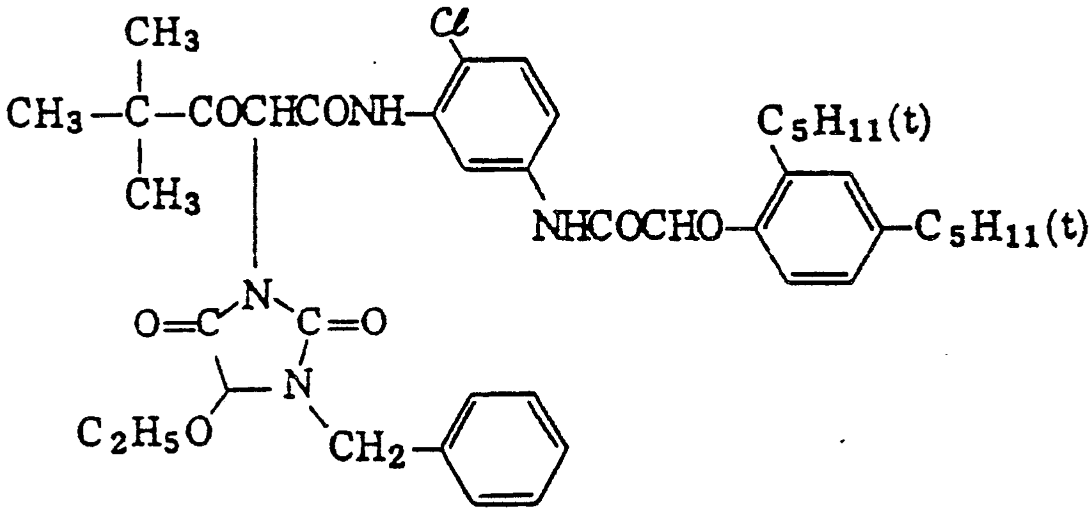
Sixth Layer (Ultraviolet Absorbing Layer)

Gelatin	0.53
Ultraviolet Absorber (UV-1)	0.02
(UV-2)	0.10
(UV-3)	0.08
Solvent (Solv-2)	0.08

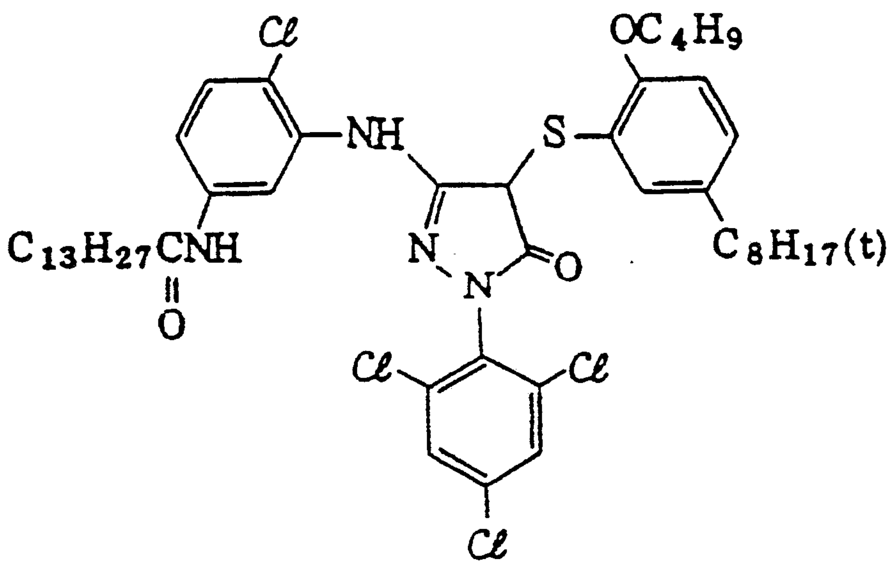
Seventh Layer (Protective Layer)

Gelatin	1.33
Acrylic modified copolymer of poly(vinyl alcohol) (17% modification)	0.17
Liquid paraffin	0.03

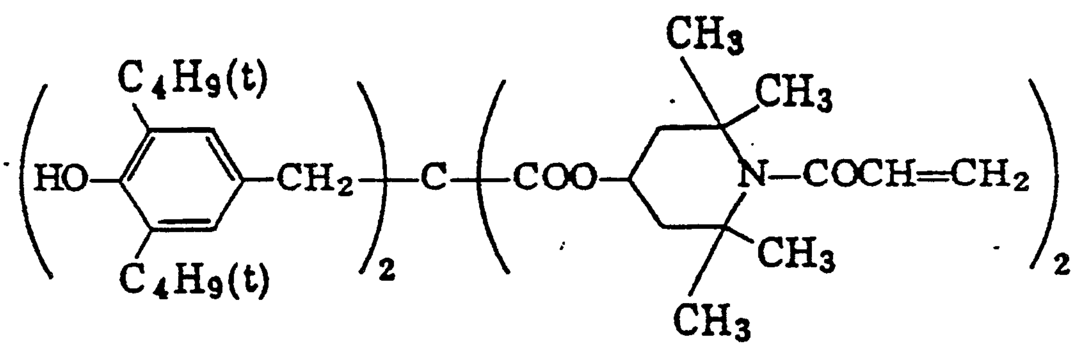
(EXY) Yellow Couper



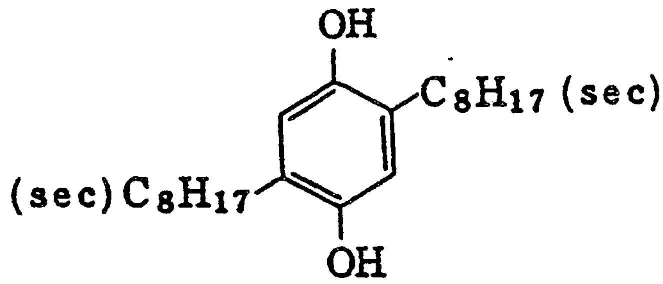
(EXM) Magenta Couper



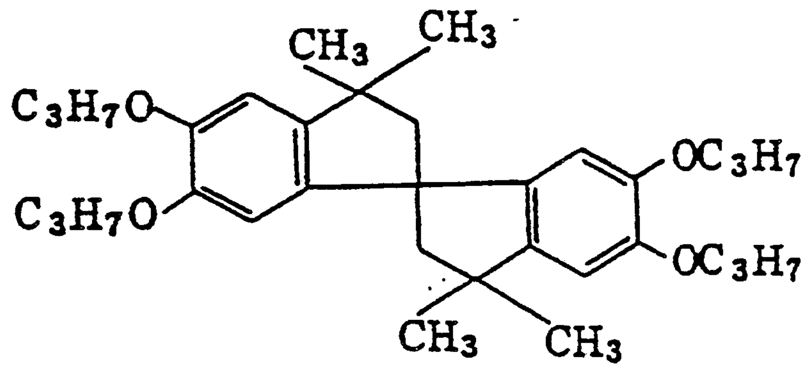
(Cpd-1) Colored Image Stabilizer



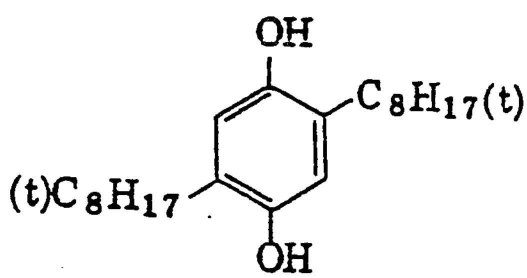
(Cpd-2) Anti-color Mixing Agent



(Cpd-3) Colored Image Stabilizer

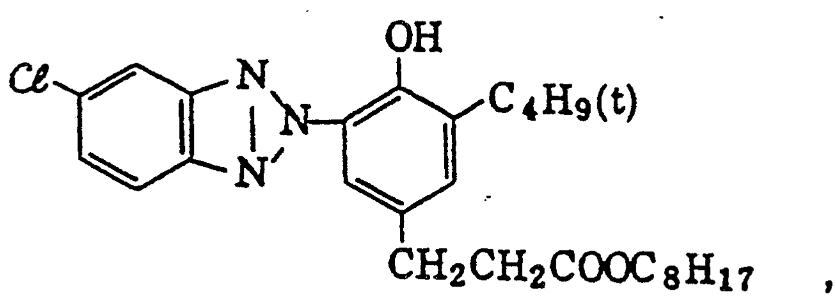


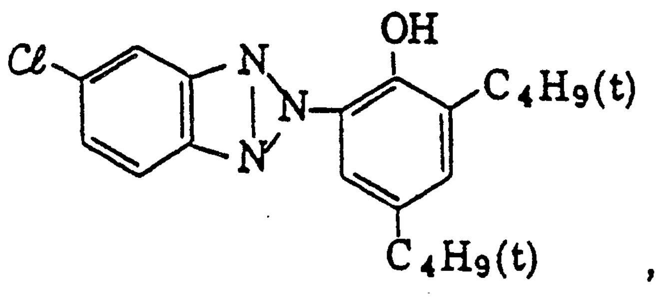
(Cpd-6) Anti-color Mixing Agent

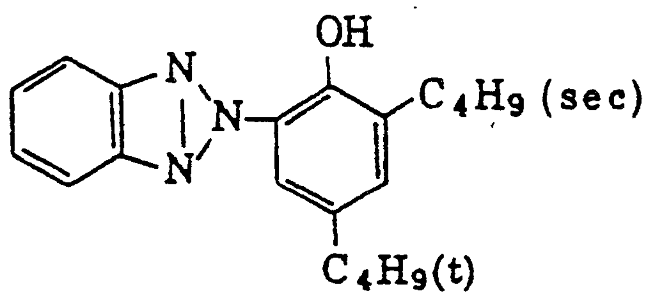


(Cpd-7) Colored Image Stabilizer

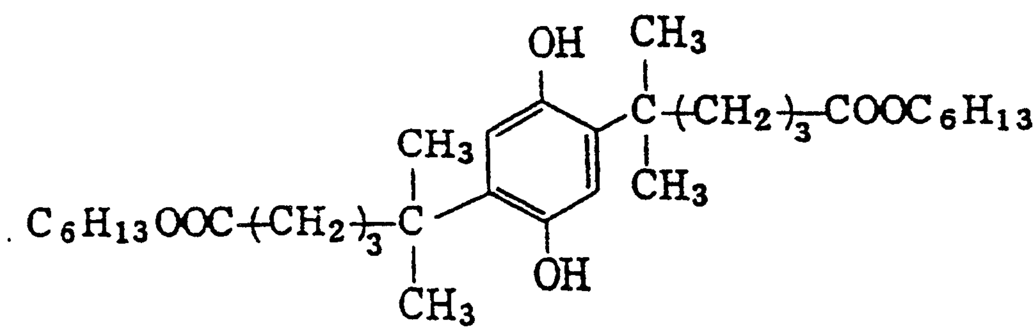
A5:8:9 (by weight) mixture of the compounds:



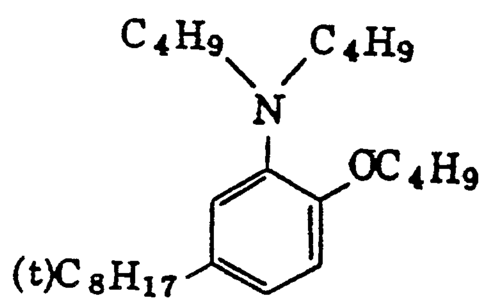




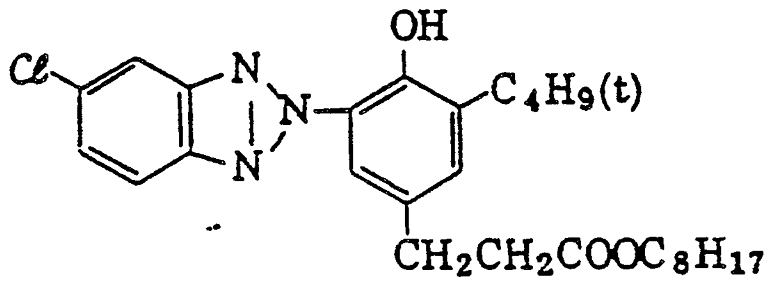
(Cpd-9) Colored Image Stabilizer



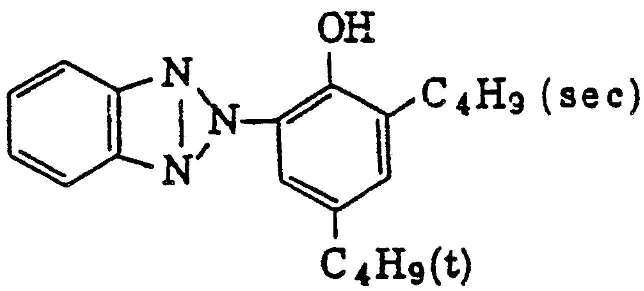
(Cpd-10) Anti-staining Agent



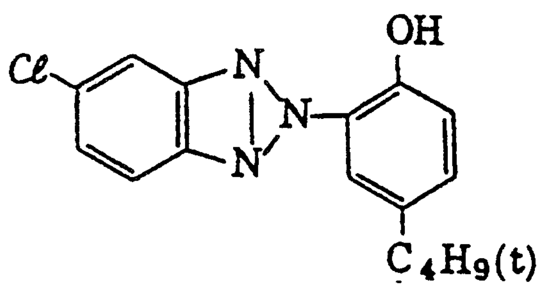
(UV-1) Ultraviolet absorber



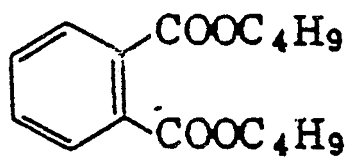
(UV-2) Ultraviolet Absorber



(UV-3) Ultraviolet Absorber



(Solv-1) Solvent

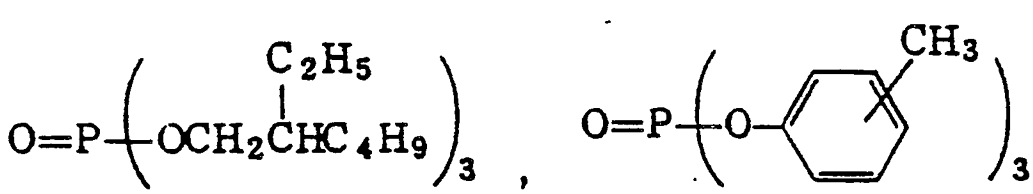


(Solv-2) Solvent

$O=P\{OoC_9H_{19}\text{-iso})_3$

(Solv-4) Solvent

A1:2 (by weight) mixture of the compounds



The silver halide emulsion for the blue sensitive emulsion layer was preferred in the way indicated below.

Solution 1

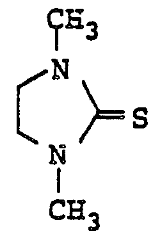
Water	1000 cc
NaCl	5.5 grams
Gelatin	25 grams

Solution 2

Sulfuric acid (1N)	20 cc

Solution 3

Silver halide solvent indicated below (1%) 2 cc



Solution 4

KBr	2.80 grams
NaCl	to make up to 140 cc

Solution 5

$AgNO_3$	5 grams
Water	to make up to 140 cc

Solution 6

KBr	67.20 grams
NaCl	8.26 grams
K_2IrCl_6(0.001%)	0.7 cc
Water	to make up to 320 cc

Solution 7

$AgNO_3$	120 grams
Water	to make up to 320 cc

Solution 1 was heated to 75°C and Solution 2 and 3 were added. Solutions 4 and 5 were then added simultaneously over a period of 9 minutes. Moreover, after a period of 10 minutes solutions 6 and 7 were added simultaneously over a period of 45 minutes. The temperature was reduced 5 minutes after the addition and the mixture was desalted. Gelatin dispersed in water was then added, the pH was adjusted to 6.2 and a mono-disperse cubic silver chlorobromide emulsion of average grain size 1.01 µm, variation coefficient (standard deviation divided by the average grain size, s/d) 0.08 which contained 80 mol% of silver bromide was obtained. Sodium thiosulfate was added to this emulsion and optimum chemical sensitization was carried out.

The silver halide emulsions for the green and red sensitive emulsion layers were prepared in the same way with different reagent quantities, temperatures and times.

The average grain sizes, variation coefficients and halide compositions of the silver halide emulsions of the blue, green and red sensitive emulsion layers are indicated in the table below.

Emulsion	Ave. Grain Size (μm)	Var. Coeff. (s/d)	Halide Composition (%)
Blue Sens.	1.01	0.08	Br = 80 Cl = 20
Green Sens.	0.45	0.10	Br = 80 Cl = 20
Red Sens.	0.40	0.10	Br = 70 Cl = 30

Samples 302 to 308 were prepared in the same way as samples 301 except that the cyan coupler in the fifth layer of sample 301 was replaced by couplers (II) and (III) of this invention and comparative compounds (I), (J), (S), (K) and (L) at the same coated coupler weight (mol per square meter), as shown in Table 4.

These samples were subjected to a color development process as indicated below after exposure through a continuous wedge.

Color Development Bath

Nitrilotriacetic acid, trisodium salt	2.0 grams
Benzyl alcohol	15 ml
Diethylene glycol	10 ml
Na_2SO_3	2.0 grams
KBr	0.5 gram
Hydroxylamine sulfate	3.0 grams
4-Amino-3-methyl-N-ethyl-N-[β-methanesulfonamido)ethyl]-p-phenylenediamine sulfate	5.0 grams
Na_2CO_3 (monohydrate)	30 grams
Water to make up to 1 liter	(pH 10.1)

Bleach-Fix Bath

Ammonium thiosulfate (70 wt%)	150 ml
Na_2SO_3	15 grams
$NH_4[Fe(EDTA)]$	55 grams
EDTA•2Na	4 grams
Water to make up to 1 liter	(pH 6.9)

Processing Operation		
	Temperature	Time
Development Bath	33° C	3 min. 30 sec.
Bleach-Fix Bath	33° C	1 min. 30 sec.
Water Wash	28-35° C	3 min.
Drying		

The cyan densities of the processed samples were measured and the results obtained were as shown in Table 4.

Table 4

Sample	Coupler (Coupler Monomer)		Chain Transfer Agent (Chain Transfer Constant)		Coupler Monomer Content of Polymer (wt%)	No. Ave. Molecular Weight	Cyan Density (Dmax)	Relative Speed*1	Remarks
301	I	(1)	$C_{12}H_{25}SH$	(3.5)	51.3	2800	2.75	0.09	This Invention
302	II	(1)	$C_{12}H_{25}SH$	(3.5)	74.2	1900	2.65	0.06	"
303	III	(2)	$C_{12}H_{25}SH$	(2.6)	50.8	2100	2.72	0.10	"
304	(I)	(1)	-	-	51.9	44000	2.01	0.00	Comparative Example
305	(J)	(1)	-	-	50.8	3700	2.50	-0.05	"
306	(S)	(1)	2-hexadecanol (About 1.0×10^{-3})		49.7	29000	2.10	0.00	"
307	(K)	(1)	-	-	74.9	15600	1.15	-0.03	"
308	(L)	(1)	-	-	75.7	3500	2.30	-0.08	"

*1: Represented by relative value of the log of the reciprocal of the exposure requried to give a density of fog + 0.5, taking the value for sample 304 to be 0.00.

It is clear from the results shown in Table 4 that the samples which contained telomeric couplers of this invention exhibited a markedly greater color forming ability and a higher speed than the samples which contained the comparative couplers (conventional polymeric couplers and couplers obtained using a chain transfer agent of which the chain transfer constant was outside the range from 0.1 to 20).

EXAMPLE 4

Samples 401 to 409 were prepared in just the same way as in Example 3 except that the magenta coupler (EXM) in the third layer of the layer structure indicated in Example 3 was replaced with couplers (XIV), (XV), (XVI) and (XVII) of this invention and comparative couplers (M), (N), (T), (0) and (P), and the colored image stabilizers and anti staining agents were added as indicated in the table below. The amount of each coupler coated (mol per square meter) was the same as in the case of coupler (EXM).

Sample	Colored Image Coupler	Anti-Staining Stabilizers	Agent
401	(XIV)	Cpd-3, Cpd-9	Cpd-10
402	(XV)	Cpd-3, Cpd-9	Cpd-10
403	(XVI)		
404	(XVII)		
405	(M)		
406	(N)		
407	(T)	Cpd-3, Cpd-9	Cpd-10
408	(O)	Cpd-3, Cpd-9	Cpd-10
409	(P)	Cpd-3, Cpd-9	Cpd-10

These samples were exposed through an optical wedge and then they were color developed and processed in the same way as in Example 3. The magenta densities of the processed samples were measured and the results obtained were as shown in Table 5.

Table 5

Sample	Coupler (Coupler Monomer)		Chain Transfer Agent (Chain Transfer Constant)		Coupler Monomer Content of Polymer (wt%)	No. Ave. Molecular Weight	Magenta Density (Dmax)	Relative Speed*1	Remarks
401	XII	(27)	$C_{12}H_{25}SH$	(2.8)	48.6	3200	2.60	0.08	This Invention
402	XI	(27)	$C_{12}H_{25}SH$	(2.8)	72.2	1900	2.15	0.06	"
403	XVI	(41)	$C_{12}H_{25}SH$	(3.7)	48.7	2600	2.40	0.04	"
404	XVII	(42)	$C_{18}H_{37}SH$	(2.5)	50.7	3000	2.20	0.04	"
405	M	(41)	-	-	50.0	36000	0.73	-0.04	Comparative Example
406	N	(41)	-	-	50.8	3500	2.09	-0.10	"
407	T	(27)	2-Hexadecanol (About 1.0×10^{-3})		50.9	20000	1.60	0.01	"
408	O	(27)	-	-	56.4	23000	1.55	-0.00	"
409	P	(27)	-	-	50.8	2500	2.20	-0.05	"

*1: Represented by relative value of the log of the reciprocal of the exposure requried to give a density of fog + 0.5, taking the value for sample 408 to be 0.

It is clear from the results shown in Table 5 that the samples which contained a telomeric coupler of this invention had a markedly higher color forming ability and a higher speed than the samples which contained the comparative couplers (conventional polymeric couplers and couplers obtained using chain transfer agents of which the chain transfer constant was outside the range from 0.1 to 20.

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

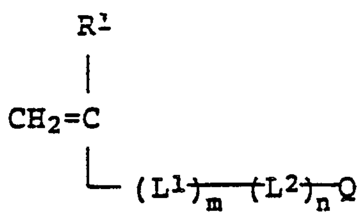
1. A silver halide color photographic material containing in at least one silver halide emulsion layer and/or in at least one layer adjacent thereto at least one lipophilic polymeric coupler, characterized in that said lipophilic polymeric coupler is obtained by a polymerization reaction using a chain transfer agent having at least 8 carbon atoms and a chain transfer constant with respect to the respective monomeric coupler in the range of from 0.1 to 20.

2. The material according to claim 1, wherein the polymeric coupler is represented by the general formula [P]:

$$E\text{-}(A)_x\text{-}(B)_y\text{-}X \quad [P]$$

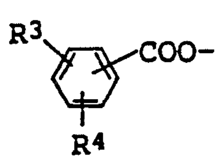
wherein E represents a univalent group having at least 8 carbon atoms and originating from the radical part which is formed by chain transfer to said chain transfer agent;
A represents a repeating unit which is derived from an ethylenically unsaturated monomer which has a coupler residual group which can couple with the oxidized form of a primary aromatic amine developing agent and form a dye;
B represents a repeating unit derived from a copolymerizable ethylenically unsaturated monomer;
X represents a univalent group;
and x and y are the contents of each type of repeating units in the polymeric coupler, the weight ratio of x and y (x:y) is from 10:90 to 100:0.

3. The material according to claim 2, wherein the repeating unit A is derived from a monomer which is represented by the general formula [I]:

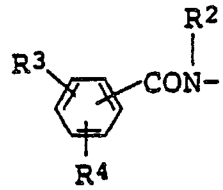


[I]

wherein Rl represents a hydrogen atom, an alkyl group whch has from 1 to 4 carbon atoms or a chlorine atom;
L^1 represents a $-CON(R^2)-$ group (where R^2 represents a hydrogen atom, an alkyl group which has from 1 to 4 carbon atoms or a substituted alkyl group which has from 1 to 6 carbon atoms), a -COO- group, an -NHCO- group, an -OCO- group, an



group (where R^3 and R^4 each independently represent a hydrogen atom, hydroxyl group, halogen atom or a substituted or unsubstituted alkyl, alkoxy, acyloxy or aryloxy group), an



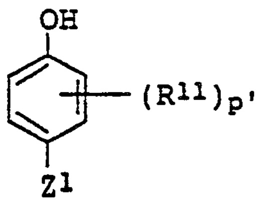
group (where R^2, R^3 and R^4 have the same meaning as above);
L^2 represents a linking group which links Q with L^1;
m represents 0 or 1;
n represents 0 or 1;
and Q represents a coupler residual group which can couple with an oxidized primary aromatic amine developing agent to form a dye.

4. The material according to claim 3, wherein the linking group represented by L^2 is represented by the formula:

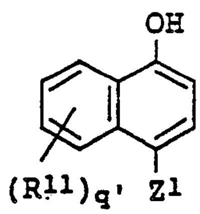
$$\{X'(J^1\text{-}X^2)_p(J^2\text{-}X^3)_q(J^3)_r\}_s$$

wherein J^1, J^2 and J3, which may be the same or different, each represent a -CO- group, $-SO_2-$ group, $-CO\overset{R^5}{N}-$ group (where R^5 represents a hydrogen atom, or a substituted or unsubstituted alkyl group which has from 1 to 6 carbon atoms), $-SO_2\overset{R^5}{N}-$ group (where R^5 has the same meanings as above), $-\overset{R^5}{N}-R^6-$ group (where R^5 has the same meanings as above and R^6 is an alkylene group which has from 1 to about 4 carbon atoms), an $-\overset{R^5}{N}-R^6-\overset{R^7}{N}-$ group (where R^5 and R^6 have the same meanings as above and R^7 represents a hydrogen atom, or a substituted or unsubstituted alkyl group which has from 1 to 6 carbon atoms), -O- group, -S- group, $-\overset{R^5}{N}-CO-\overset{R^7}{N}-$ group (where R^5 and R^7 have the same meanings as above), $-\overset{R^5}{N}-SO_2-\overset{R^7}{N}-$ group (where R^5 and R^7 have the same meanings as above), -COO-group, -OCO-group, $-\overset{R^5}{N}CO-$ group (where R^5 has the same meanings as above);
X^1, X^2 and X^3, which may be the same or different, each represents a substituted or unsubstituted alkylene group, a substituted or unsubstituted arylene group, or a substituted or unsubstituted aralkylene group;
and p, q, r and s each represent 0 or 1.

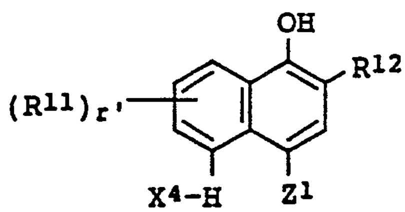
5. The material according to claims 3 and 4, wherein the coupler residual group represented by Q is derived from a cyan forming phenol type coupler compound which is represented by the general formulae [II] and [V] or is derived from a cyan forming naphthol type coupler compound which is represented by the general formulae [III] and [IV] (these compounds loose a hydrogen atom other than the hydroxyl hydrogen atom and link-up with the $(L^1)_m(L^2)_n$ group):



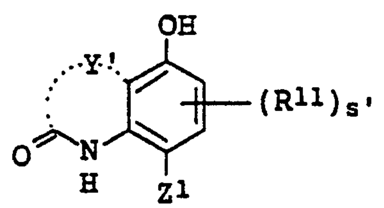
[II]



[III]



[IV]



[V]

wherein R^{11} represents a group which can be substituted on a phenol ring or a naphthol ring, and which has from 0 to 30 carbon atoms;

R^{12} represents a $-CONR^{14}R^{15}$ group, $-NHCOR^{14}$ group, $-NHCOOR^{16}$ group, $-NHSO_2R^{16}$ group, $-NHCONR^{14}R^{15}$ group or $-NHSO_2R^{14}R^{15}$ group, (wherein R^{14} and R^{15} each represents a hydrogen atom, an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms or a heterocyclic group which has from 2 to 30 carbon atoms, and R^{16} represents an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms, or a heterocyclic group and R^{14} and R^{15} may be joined together to form a heterocyclic ring);

p' is an integer of from 0 to 3;

s' is an integer of from 0 to 2;

q' and r' are each integers of from 0 to 4;

X4 represents an oxygen atom, a sulfur atom or an

$R^{17}N<$

group (where R^{17} represents a hydrogen atom or a univalent group);

Z^1 represents a hydrogen atom or a group which can be eliminated by a coupling reaction with the oxidized form of a primary aromatic amine;

and Y′ represents a group of atoms which is required to form, together with the carbon atoms to which it is bound, a five to seven-membered ring.

6. The material according to claim 5, wherein the groups represented by R^{11} are halogen atoms, aliphatic groups, carbonamido groups, or sulfonamido groups.

7. The material according to claims 5 and 6, wherein R^{12} represents a $-CONR^{14}R^{15}$ group.

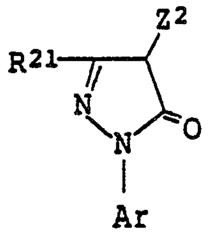
8. The material according to any one of claims 5 to 7, wherein X^4 represents a

$R^{17}N\langle$

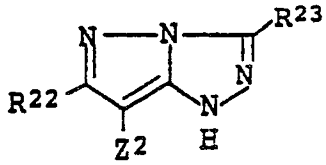
group.

9. The material according to any one of claims 5 to 8, wherein Z^1 represents a hydrogen atom, a halogen atom, an aliphatic oxy group, an aromatic oxy group, a heterocyclic thio group or an aromatic azo group.

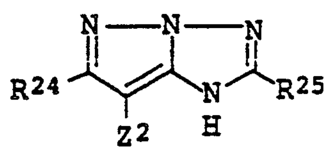
10. The material according to claims 3 and 4, wherein the coupler residual group represented by Q is derived from a magenta color forming coupler compound represented by the general formulae [VI], [VII], [VIII], [IX], [X], [XI], and [XII], (linked by $-(L^1)_m-(L^2)_n-$ in any of Ar, Z^2, R^{21} to R^{33}):



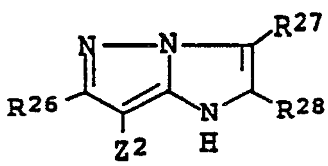
[VI]



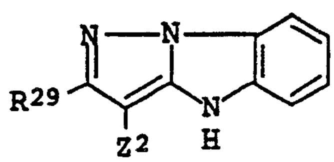
[VII]



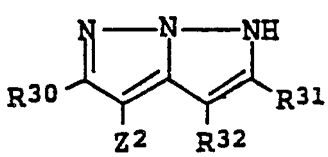
[VIII]



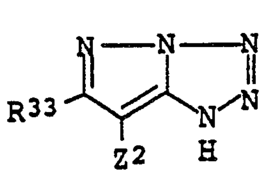
[IX]



[X]



[XI]



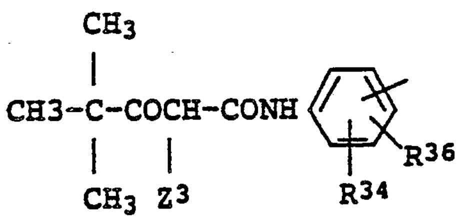
[XII]

wherein Ar represents a substituent group of the known type in the 1-position of a 2-pyrazolin-5-one coupler; R^{21} represents an unsubstituted anilino group, an acylamino group; or a ureido group;
R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}, R^{28}, R^{29}, R^{30}, R^{31}, R^{32} and R^{33} each represenr a hydrogen atom or a hydroxyl group, or they may be each represent an unsubstituted or a substituted alkyl group, an aryl group, a heterocyclic group, an alkylamino group, an acylamino group, an anilino group, an alkoxycarbonyl group, an alkylcarbonyl group, an arylcarbonyl group, an alkylthio group, an arylthio group, a carbamoyl group, a sulfamoyl group, or a sulfonamido group;

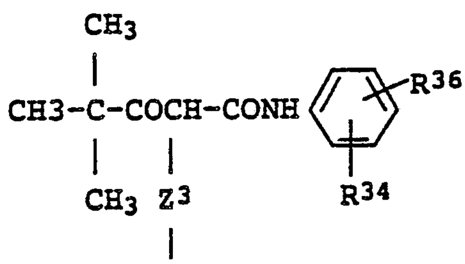
and Z^2 represents a hydrogen atom or a group which can be eliminated by a coupling reaction with the oxidized form of a primary aromatic amine developing agent.

11. The material according to claim 10, wherein the group which can be eliminated and as represented by Z^2 is a halogen atom, a coupling elimination group which is linked with an oxygen atom or a coupling elimination group which is linked with a nitrogen atom, preferably an alkyloxy group, a chlorine atom, a pyrazolyl group, an imidazolyl group or a triazolyl group.

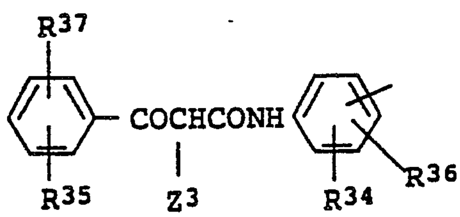
12. The material according to claims 3 to 4, wherein the coupler residual group represented by Q is derived from a yellow color forming acylacetamide type coupler compound which is represented by the general formulae [XIII], [XIII'], [XIV], [XIV'], [XV] and [XV'] (the free bonds shown in the general formulae are linked to the - $L^1)_m$-$(L^2)_n$- group):



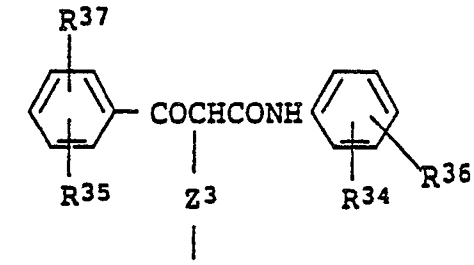
[XIII]



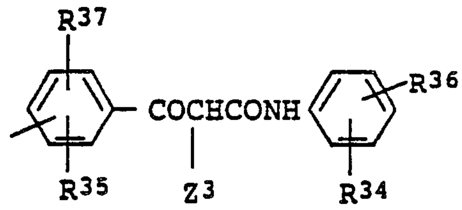
[XIII']



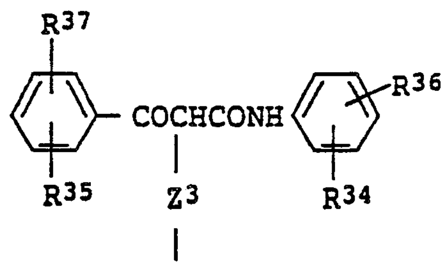
[XIV]



[XIV']



[XV]

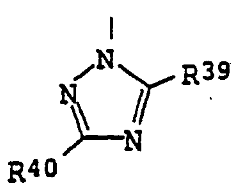


[XV']

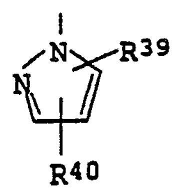
wherein R^{34}, R^{35}, R^{36} and R^{37} each represent a hydrogen atom or a known substituent group for a yellow color forming coupler residual group;
Z^3 is a hydrogen atom or a group which is represented by the general formulae [XVI], [XVII], [XVIII] or [XIX] as indicated below:

$-OR^{38}$ [XVI]

wherein R^{38} represents a heterocyclic group or an alkyl group which may be substituted;

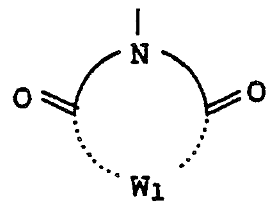


[XVI]



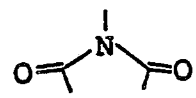
[XVII]

wherein R^{39} and R^{40} each represent a hydrogen atom, halogen atom, carboxylic acid ester group, amino group, alkyl group, alkylthio group, alkoxy group, alkylsulfonyl group, alkylsulfinyl group, carboxylic acid group, sulfonic acid group, unsubstituted or substituted phenyl group or a heterocyclic group, and these groups may be the same or different;



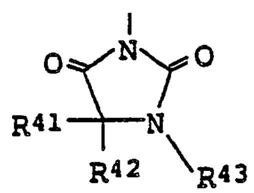
[XIX]

wherein W_2 is a group of non-metal atoms required to form a four, five or six-membered ring together with the

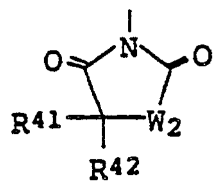


part shown in the formula.

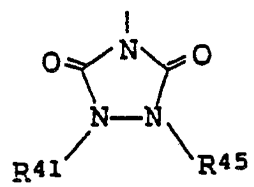
13. The material according to claim 12, wherein the group represented by the.general formula [XIX] is a group represented by the general formulae [XX] to [XXII]:



[XX]



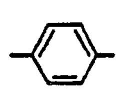
[XXI]



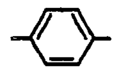
[XXII]

wherein R^{41} and R^{42} each represents a hydrogen atom, alkyl group, aryl group, alkoxy group, aryloxy group or a hydroxyl group;
R^{43}, R^{44} and R^{45} each represent a hydrogen atom, alkyl group, aryl group, aralkyl group or an acyl group; and W_2 represents an oxygen atom or a sulfur atom.

14. The material according to any one of claims 3 to 13, wherein in the general formula [I],
R^1 represents a hydrogen atom or a methyl group;
L^1 represents -CONH, -COO-, -OCO-,



COO- or



CONNH-;
m represents 1;
and n represents 0 or 1.

15. The material according to any one of claims . 4 to 14, wherein L^2 is represented by the formula

$$\{X^1(J^1\text{-}X^2)_p(J^2\text{-}X^3)_q(J^3)_r\}_s$$

wherein J^1, J^2 and J^3, which may be the same or different, each represent -CO-, $-SO_2-$, -CONH-, $-SO_2NH-$, -NHCO , $-NHSO_2-$, -O-, -NHCONH-, -S-, COO-, -OCO-, -NHCOO- or -OCONH;
X^1, X^2 and X^3, which may be the same or different, each represent an alkylene group which has from 1 to 4 carbon atoms, an arylene group, or a substituted arylene group;
and p, q, r and s each represent 0 or 1.

16. The material according to any one of claims 2 to 15, wherein in the aforementioned general formula [P], E represents a univalent group which is represented by the general formula [XXII]:

$E^1(Y)_p$ [XXII]

wherein E^1 represents an alkyl group, substituted alkyl group, substituted aryl group, substituted naphthyl group;
Y represents -S-, -SO- or $-SO_2$;
and p represents 0 or 1.

17. The material according to any one of claims 2 to 16, wherein in the general formula [P], X represents a hydrogen atom or a halogen atom.

18 The material according to any one of claims 1 to 17, wherein the number average molecular weight of the polymeric coupler is from about 500 to about 10,000, in particular from about 500 to about 5,000.

19. A method of forming a color image which comprises developing an imagewise exposed silver halide color photographic material with a color developing composition containing a primary aromatic amine based color developing agent as the main component, characterized in that a silver halide color photographic material according to any one of claims 1 to 18 is used.