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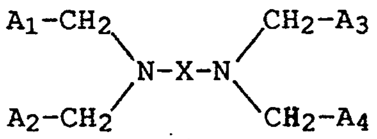
(54) Bleaching solution for light-sensitive silver halide color photographic material and processing method using the same.

(57) Disclosed are a bleaching solution for a light-sensitive silver halide color photographic material comprising at least 0.10 mole/ℓ of a ferric complex salt of a compound represented by the following formula (A) and 50 mole % or less of total cations being ammonium ions,



(A)

wherein A$_1$ to A$_4$ may be the same or different, respectively and represent -CH$_2$OH, -COOM or -PO$_3$M$_1$M$_2$ where M, M$_1$ and M$_2$ each represent a hydrogen atom, sodium, potassium or ammonium; and X represents a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms and a total carbon number including a branched part is 3 or more,
and a processing method of a light-sensitive silver halide color photographic material using the same.

EP 0 450 293 A2

Rank Xerox (UK) Business Services

BLEACHING SOLUTION FOR LIGHT-SENSITIVE SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL AND PROCESSING METHOD USING THE SAME

BACKGROUND OF THE INVENTION

This invention relates to a bleaching solution for a light-sensitive silver halide color photographic material and a processing method using said bleaching solution, more particularly to a bleaching solution for a light-sensitive silver halide color photographic material by which bleaching fog can be effectively inhibited, and a processing method using said bleaching solution.

A processing of a light-sensitive material basically comprises two steps of color developing and desilvering, and desilvering comprises bleaching and fixing steps or a bleach-fixing step. As other additional processing steps than these steps, a rinsing processing and a stabilizing processing are added.

In a processing solution having bleachability to be used for a desilvering step of a light-sensitive silver halide color photographic material, as an oxidizing agent for bleaching image silver, inorganic oxidizing agents such as prussiate and bichromate have been widely used.

However, some serious drawbacks have been pointed out in processing solutions containing these inorganic oxidizing agents and having bleachability. For example, although prussiate and bichromate are relatively excellent in the point of a bleaching power of image silver, they have a fear of forming a cyan ion or a hexavalent chromium ion which are decomposed by light and become harmful to human bodies, and therefore have undesirable properties in the point of preventing pollution. Further, the processing solutions containing these inorganic oxidizing agents have a drawback that it is difficult to regenerate them without discarding a waste liquor after processing.

To the contrary, as a processing solution having few problems in pollution and satisfying demands such as rapid processing, simple processing and regeneration of a waste liquor, a processing solution containing as an oxidizing agent a metal complex salt of an organic acid such as a metal complex salt of an aminopolycarboxylic acid has been used. However, the processing solution using a metal complex salt of an organic acid has a poor oxidizing power, and therefore has a drawback that a bleaching rate (oxidizing rate) of image silver (metal silver) formed during a developing step is slow. For example, an iron (III) complex salt of ethylenediaminetetraacetic acid which is considered to have a strong bleaching power among metal complex salts of an aminopolycarboxylic acid has been practically utilized in part as a bleaching solution and a bleach-fixing solution. However, it has a drawback that it is insufficient in a bleaching power in the case of a high sensitivity light-sensitive silver halide color photographic material mainly composed of a silver chloride, silver bromide, silver chlorobromide or silver iodobromide emulsion, particularly a color paper for photographing which contain silver iodide as silver halide and are high in silver quantity, a color negative film for photographing and a color reversal film, and therefore a bleaching step requires a long period of time.

Further, in a development processing method in which a large quantity of light-sensitive silver halide photographic materials are processed continuously by an automatic processor, for avoiding worsening of properties of a bleaching solution caused by change in concentrations of respective components, a means for maintaining concentrations of respective components of a processing solution within a predetermined range is required. As such a means, in recent years, from the standpoints of economy and pollution, there have been proposed a so-called high concentration and low replenishment system in which these replenishing solutions are concentrated and replenished in small amounts or a method in which a regenerating agent is added to an overflow solution and the solution obtained is used again as a replenishing solution. Particularly, as to a bleaching solution, there has been utilized practically a method in which a ferrous organic acid complex salt generated by bleaching developed silver, for example, an iron (II) complex salt of ethylenediaminetetraacetic acid is oxidized by aeration to be converted into an iron (III) complex salt of ethylenediaminetetraacetic acid, namely, a ferric organic acid complex salt, further, a regenerating agent for supplementing insufficient components is added thereto, and the solution obtained is used again as a replenishing solution.

However, in recent years, for processing a light-sensitive silver halide color photographic material in a shorter time and reducing a cost for collection and delivery, a number of so-called compact laboratories (another name: miniature laboratories) have increased. In such laboratories, simplification of processing and reduction in area for setting a developing machine are highly demanded and complicated handlings and controls are required, and therefore a regenerating processing which requires a space for the processing is not preferred.

Accordingly, a high concentration and low replenishment system in which low replenishment is carried out without carrying a regenerating processing is preferred. However, when a replenishing amount of a bleaching solution is reduced extremely, concentrations of components of a color developing solution brought into a bleaching solution are elevated, and also influence of condensation due to evaporation is liable to be exerted, whereby components of a color developing solution is accumulated increasingly. Thus, when concentrations of components of a color developing solution in a bleaching solution are elevated, mixing ratios of a color developing agent and a sulfite which are reductive components are increased, whereby there are drawbacks that a bleaching reaction is inhibited and that as a more serious problem, bleaching fog is liable to be generated.

The bleaching fog has been increased in the recent low replenishment of a bleaching solution, and a trouble of tar generation in a bleaching tank of an automatic processor tends to occur.

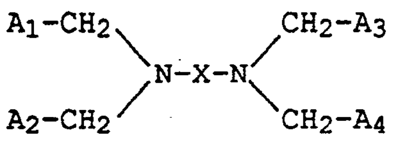
Thus, in recent years, since low pollution and low cost are requested, further lower replenishment has been demanded. Further, it has been demanded that rapid processing services to return films to users as quickly as possible after receipt of them are made in the above compact laboratories where a processing quantity is relatively small in general, and a regenerating rate of a tank solution is low. Under such a situation, the problems described above have become more serious.

SUMMARY OF THE INVENTION

Accordingly, a first object of the present invention is to provide a bleaching solution for a light-sensitive silver halide color photographic material which enables rapid processing and low replenishment, and yet is improved in bleaching fog, and a processing method using the same.

Further, a second object of the present invention is to provide a bleaching solution for a light-sensitive silver halide color photographic material which is excellent in processing stability and enables both of continuous processing and processing of a small quantity over a long period of time, and a processing method using the same.

The above objects of the present invention can be accomplished by a bleaching solution for a light-sensitive silver halide color photographic material comprising at least 0.10 mole/ℓ of a ferric complex salt of a compound represented by the following formula (A) and ammonium ions with an amount of 50 mole % or less based on total cations, and a method for processing a light-sensitive silver halide color photographic material using said bleaching solution.



(A)

wherein A_1 to A_4 may be the same or different, respectively and each represent -CH_2OH, -COOM or -$PO_3M_1M_2$ where M, M_1 and M_2 each represent a hydrogen atom, sodium, potassium or ammonium; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms and a total carbon number including a branched part is 3 or more.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following, the present invention is explained in more detail.

Preferred embodiments are the above bleaching solution having a pH of 2.0 to 5.5 and the method for processing a light-sensitive silver halide color photographic material using the bleaching solution. Further, the bleaching solution in which an amount of ammonium ions is 20 mole % or less based on the total cations in the above bleaching solution and the processing method using the bleaching solution are also a preferred embodiment. Furthermore, the bleaching solution in which an amount of ammonium ions is 0 to 10 mole % or less based on the total cations in the above bleaching solution and the processing method using the bleaching solution are also a preferred embodiment of the present invention. It is a preferred embodiment that a replenishing amount of the bleaching solution is 20 to 400 ml/m^2 per 1 m^2 of a light-sensitive material since the effect of the present invention can be exhibited remarkably.

The bleaching solution containing a ferric complex salt of a compound represented by the formula (A) in the present invention has been known in Japanese Unexamined Patent Publication No. 222252/1987, and the fact that bleaching fog is liable to be generated has been also known in the above Japanese Publication. Further, the fact that bleaching fog can be prevented by making a pH of a bleaching solution 2.5 to 5.5 has been also known in Japanese Unexamined Patent Publication No. 44352/1990. However, in the known examples as described above, bleaching fog cannot be prevented completely by making a pH of a bleaching solution lower. When a bleaching solution is replenished with a smaller amount, further when a processing quantity is small, bleaching fog becomes more significant.

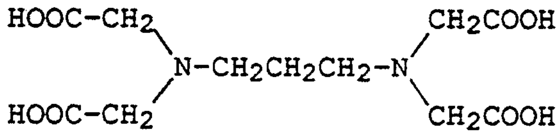
The present inventors have found that the above bleaching fog is liable to be generated by a bleaching power of a ferric complex salt of the formula (A) and that the bleaching fog is further liable to be generated by using a ferric complex salt together with ammonium ions, to accomplish the present invention.

In the following, the compound represented by the formula (A) is described in detail.

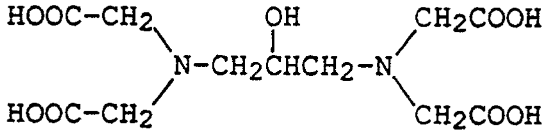
A_1 to A_4 may be the same or different, respectively and represent $-CH_2OH$, $-COOM$ or $-PO_3M_1M_2$ where M, M_1 and M_2 each represent a hydrogen atom, sodium, potassium or ammonium; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms (e.g. propylene, butylene and pentamethylene).

As the substituent group, there may be mentioned a hydroxyl group and a lower alkyl group having 1 to 3 carbon atoms. Preferred specific examples of the compound represented by the above formula (A) are shown below.

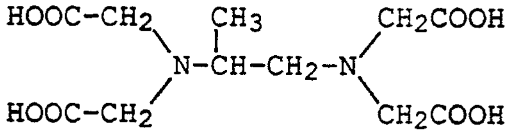
(A - 1)



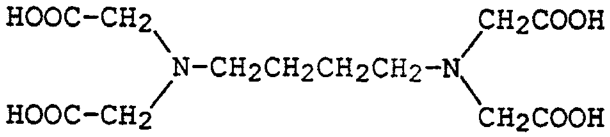
(A - 2)



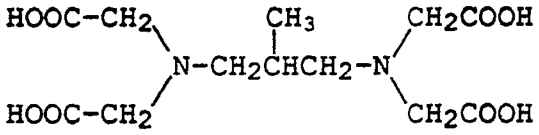
(A - 3)



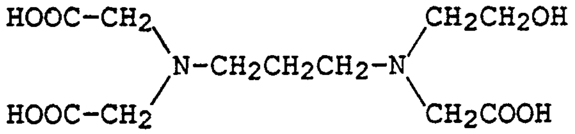
(A - 4)



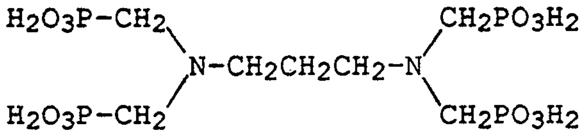
(A - 5)



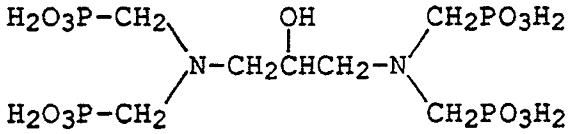
(A - 6)



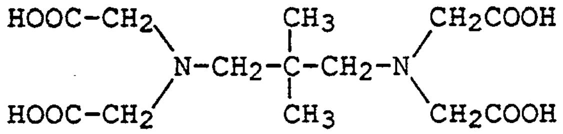
(A - 7)



(A - 8)



(A - 9)



In addition to these compounds (A - 1) to (A - 9), a sodium salt, a potassium salt or an ammonium salt of them can be used as desired. However, when a large amount of an ammonium salt is used, bleaching fog is liable to be generated, whereby an ammonium salt of a ferric complex salt is used in an amount of 50 mole % or less, preferably 20 mole % or less, more preferably 0 to 10 mole % based on the total cations for preventing bleaching fog.

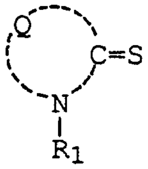
Among the above exemplary compounds, those particularly preferably used in the present invention are (A - 1), (A - 4), (A - 7) and (A - 8), particularly preferably (A - 1).

A ferric complex salt of the compound represented by the above formula (A) is used in an amount of at least 0.10 mole per liter of a bleaching solution, preferably in the range of 0.15 mole to 0.6 mole, more preferably in the range of 0.18 mole to 0.5 mole.

In the bleaching solution of the present invention, in combination with a ferric complex salt of the compound represented by the above formula (A), other ferric complex salts of an aminopolycarboxylic acid (e.g. a ferric complex salt of ethylenediaminetetraacetic acid, a ferric complex salt of diethylenetriaminepentaacetic acid, a ferric complex salt of 1,2-cyclohexanediaminetetraacetic acid and a ferric complex salt of glycol ether diaminetetraacetic acid) can be combinedly used.

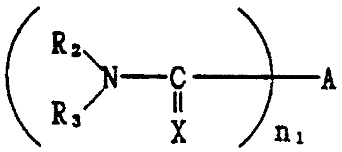
However, for exhibiting the effect of the present invention more favorably, preferred is a bleaching solution in which substantially only a ferric complex salt of the compound represented by the above formula (A) is used. Here, "substantially" means at least 70 % or more (calculated in terms of mole) based on all ferric complex salts. Said ratio is preferably 80 % or more, more preferably 90 % or more, most preferably 95 % or more.

The bleaching solution according to the present invention preferably contains imidazole and a derivative thereof or at least one compound represented by the following formulae (I) to (IX), whereby the effect of the present invention can be exhibited more favorably. Further, since another effect that precipitation caused by silver in the bleaching solution is reduced can be obtained, the above compounds are used preferably in the present invention.



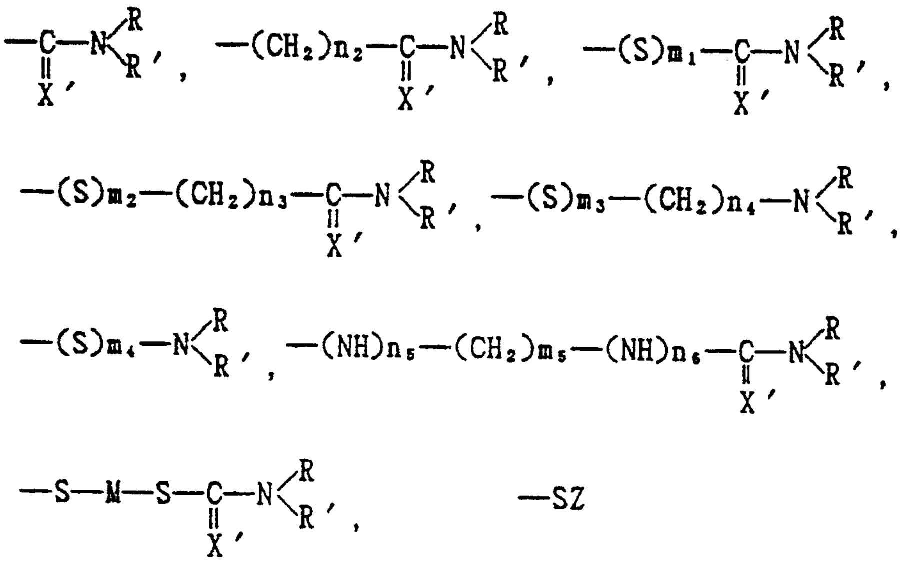
(I)

wherein Q represents a group of atoms necessary for forming a nitrogen-containing hetero ring (including those to which a 5 or 6-membered unsaturated ring is fused); and R_1 represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group, an aryl group, a heterocyclic group (including those to which a 5 or 6-membered unsaturated ring is fused) or an amino group.



(II)

wherein R_2 and R_3 each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxy group, a carboxy group, an amino group, an acyl group having 1 to 3 carbon atoms, an aryl group or an alkenyl group; A represents



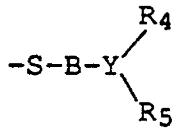
$$-\underset{\underset{X'}{\|}}{C}-N\begin{smallmatrix}R\\R'\end{smallmatrix},\quad -(CH_2)_{n_2}-\underset{\underset{X'}{\|}}{C}-N\begin{smallmatrix}R\\R'\end{smallmatrix},\quad -(S)_{m_1}-\underset{\underset{X'}{\|}}{C}-N\begin{smallmatrix}R\\R'\end{smallmatrix},$$

$$-(S)_{m_2}-(CH_2)_{n_3}-\underset{\underset{X'}{\|}}{C}-N\begin{smallmatrix}R\\R'\end{smallmatrix},\quad -(S)_{m_3}-(CH_2)_{n_4}-N\begin{smallmatrix}R\\R'\end{smallmatrix},$$

$$-(S)_{m_4}-N\begin{smallmatrix}R\\R'\end{smallmatrix},\quad -(NH)_{n_5}-(CH_2)_{m_5}-(NH)_{n_6}-\underset{\underset{X'}{\|}}{C}-N\begin{smallmatrix}R\\R'\end{smallmatrix},$$

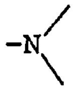
$$-S-M-S-\underset{\underset{X'}{\|}}{C}-N\begin{smallmatrix}R\\R'\end{smallmatrix},\qquad -SZ$$

or an n_1-valent heterocyclic residue (including those to which a 5 or 6-membered unsaturated ring is fused); X represents =S, =O or =NR"; where R and R' have the same meanings as R_2 and R_3, respectively; X' has the same meaning as X; Z represents a hydrogen atom, an alkali metal atom, an ammonium group, an amino group, a nitrogen-containing heterocyclic residue, an alkyl group or

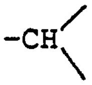


$$-S-B-Y\begin{matrix}R_4\\R_5\end{matrix} \quad ;$$

M represents a divalent metal atom; R" represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group, an aryl group, a heterocyclic residue (including those to which a 5 or 6-membered unsaturated ring is fused) or an amino group; n_1 to n_6 and m_1 to m_5 each represent an integer of 1 to 6; B represents an alkylene group having 1 to 6 carbon atoms; Y represents



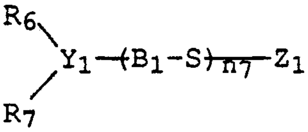
$$-N< \quad \text{or}$$



$$-CH< \quad ;$$

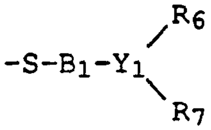
R_4 and R_5 have the same meanings as R_2 and R_3, respectively, provided that R_4 and R_5 may each represent -B-SZ; and R_2 and R_3, R and R' and R_4 and R_5 each may be bonded to form a ring.

The compound represented by the formula (II) may include an enolized product and a salt thereof.



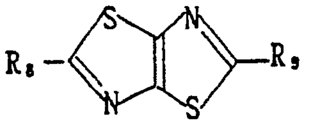
$$\begin{matrix}R_6\\R_7\end{matrix}Y_1-(B_1-S)_{n_7}-Z_1 \qquad (III)$$

wherein R_6 and R_7 each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxy group, a carboxy group, an amino group, an acyl group having 1 to 3 carbon atoms, an aryl group, an alkenyl group or $-B_1-S-Z_1$; R_6 and R_7 may be bonded to form a ring; Y_1 represents >N- or >CH-; B_1 represents an alkylene group having 1 to 6 carbon atoms; Z_1 represents a hydrogen atom, an alkali metal atom, an ammonium group, an amino group, a nitrogen-containing heterocyclic residue or



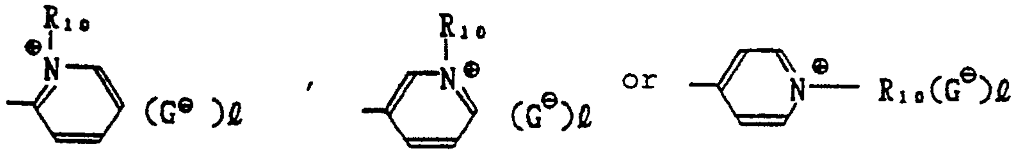
$$-S-B_1-Y_1\begin{matrix}R_6\\R_7\end{matrix} \quad ;$$

and n_7 represents an integer of 1 to 6.

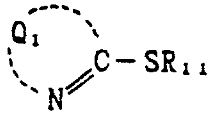


(IV)

wherein R_8 and R_9 each represent

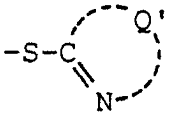


where R_{10} represents an alkyl group or $-(CH_2)n_8SO_3$-provided that when R_{10} is $-(CH_2)n_8SO_3^-$, ℓ represents 0, and when R_{10} is an alkyl group, ℓ represents 1; G^-represents an anion; and n_8 represents an integer of 1 to 6.

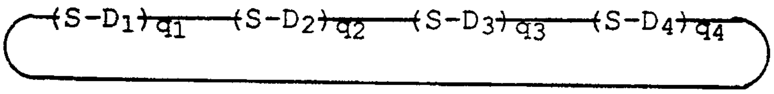


(V)

wherein Q_1 represents a group of atoms necessary for forming a nitrogen-containing hetero ring (including those to which a 5 or 6-membered unsaturated or saturated ring is fused); and R_{11} represents a hydrogen atom, an alkali metal atom,

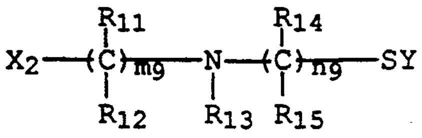


or an alkyl group where Q' has the same meaning as Q_1.



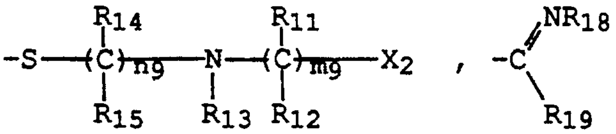
(VI)

wherein D_1, D_2, D_3 and D_4 each represent a mere bonding arm, an alkylene group having 1 to 8 carbon atoms or a vinylene group; q_1, q_2, q_3 and q_4 each represent 0, 1 or 2; and a ring formed together with sulfur atoms may be further fused to a 5 or 6-membered saturated or unsaturated ring.



$$X_2-\left(\underset{R_{12}}{\overset{R_{11}}{C}}\right)_{m_9}-\underset{R_{13}}{N}-\left(\underset{R_{15}}{\overset{R_{14}}{C}}\right)_{n_9}-SY \qquad \text{(VII)}$$

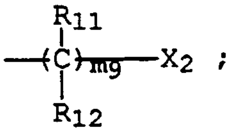
wherein X_2 represents $-COOM'$, $-OH$, $-SO_3M'$, $-CONH_2$, $-SO_2NH_2$, $-NH_2$, $-SH$, $-CN$, $-CO_2R_{16}$, $-SO_2R_{16}$, $-OR_{16}$, $-NR_{16}R_{17}$, $-SR_{16}$, $-SO_3R_{16}$, $-NHCOR_{16}$, $-NHSO_2R_{16}$, $-OCOR_{16}$ or $-SO_2R_{16}$; Y_2 represents



$$-S-\left(\underset{R_{15}}{\overset{R_{14}}{C}}\right)_{n_9}-\underset{R_{13}}{N}-\left(\underset{R_{12}}{\overset{R_{11}}{C}}\right)_{m_9}-X_2 \quad , \quad -C\begin{matrix}\nearrow NR_{18}\\ \searrow R_{19}\end{matrix}$$

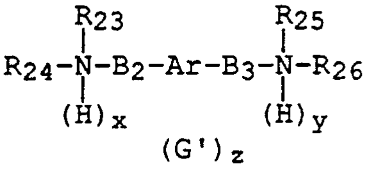
or a hydrogen atom;

m_9 and n_9 each represent an integer of 1 to 10; R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{17} and R_{18} each represent a hydrogen atom, a lower alkyl group, an acyl group or



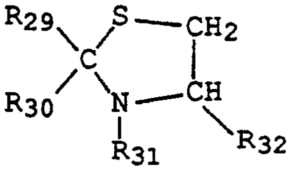
$$-\left(\underset{R_{12}}{\overset{R_{11}}{C}}\right)_{m9}-X_2\ ;$$

where R_{16} represents a lower alkyl group; R_{19} represents $-NR_{20}R_{21}$, $-OR_{22}$ or $-SR_{22}$; R_{20} and R_{21} each represent a hydrogen atom or a lower alkyl group; R_{22} represents a group of atoms necessary for forming a ring by bonding to R_{18}; R_{20} or R_{11} may be bonded to R_{18} to form a ring; and M' represents a hydrogen atom or a cation.



$$R_{24}-\underset{(H)_x}{\overset{R_{23}}{N}}-B_2-Ar-B_3-\underset{(H)_y}{\overset{R_{25}}{N}}-R_{26}\quad (G')_z \qquad \text{(VIII)}$$

wherein Ar represents a divalent aryl group or a divalent organic group in which an aryl group is combined with an oxygen atom and/or an alkylene group; B_2 and B_3 each represent a lower alkylene group; R_{23}, R_{24}, R_{25} and R_{26} each represent a hydroxy-substituted lower alkyl group; x and y each represent 0 or 1; G' represents an anion; and z represents 0, 1 or 2.



(IX)

wherein R_{29} and R_{30} each represent a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; R_{31} represents a hydrogen atom or an alkyl group; and R_{32} represents a hydrogen atom or a carboxy group.

As representative specific examples of the compounds represented by the above formulae (I) to (IX), and imidazole and a derivative thereof, there may be mentioned (I-1) to (I-10), (II-1) to (II-27), (III-1) to (III-15), (IV-1) to (IV-3), (V-1) to (V-23), (VI-1) to (VI-17), (VII-1) to (VII-15), (VIII-1) to (VIII-7), (IX-1) to (IX-5) and (A-1) to (A-8) described on p. 17 to p. 39 of Japanese Patent Application No. 32501/1988.

These compounds are compounds generally used as a bleaching accelerator, and hereinafter called as the bleaching accelerators of the present invention.

These bleaching accelerators may be used singly or in combination of two or more kinds, and the amount to be added is generally in the range of about 0.01 to 100 g per liter of the bleaching solution for obtaining good results. However, generally speaking, when the amount to be added is extremely small, a bleaching accelerating effect is small, and when the amount to be added is unnecessarily and extremely large, precipitation occurs, whereby a light-sensitive silver halide color photographic material processed may be stained in some cases. Accordingly, it is preferably 0.05 to 50 g, more preferably 0.05 to 15 g per liter of the bleaching solution.

When the bleaching accelerator is added, it may be added as such and dissolved, but in general, it may be previously dissolved in water, an alkali or an organic acid and then added, and if necessary, it can be dissolved by using an organic solvent such as methanol, ethanol and acetone and then added.

The bleaching solution of the present invention is preferably used at pH 2.0 to 5.5, more preferably pH 3.0 to 5.0. If the pH of the bleaching solution is more than 5.5, bleaching fog cannot be prevented sufficiently. On the other hand, if the pH is less than 2.0, bleaching fog can be prevented, but influence may be exerted on photographic performances. Processing is carried out preferably at a temperature of 20 °C to 45 °C, more desirably 25 °C to 42 °C.

To the bleaching solution of the present invention, a halide such as ammonium bromide is generally added.

In the bleaching solution of the present invention, pH buffering agents comprising boric acid or various salts such as borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide can be contained singly or in combination of two or more kinds. Further, various fluorescent brighteners, anti-forming agents, surfactants and antifungal agents can be also contained.

In the bleaching solution of the present invention, when 50 mole % or less, preferably 20 mole %, particularly preferably 10 mole % or less of total cations is ammonium ions, prevention of bleaching fog which is the effect of the present invention can be effectively accomplished.

The replenishing amount of the bleaching solution according to the present invention is preferably 20 ml to 400 ml, more preferably 30 ml to 350 ml, particularly preferably 40 ml to 300 ml, most preferably 50 ml to 250 ml per 1 m^2 of a light-sensitive silver halide color photographic material.

The bleaching solution described above is used immediately after color development during processing steps.

In the present invention, from the standpoint of rapid processing, processing is preferably carried out by a bleaching solution and subsequently by a fixing solution or a bleach-fixing solution.

Preferred specific processing steps of the processing method according to the present invention are shown below.

(1) Color developing → bleaching → fixing → washing
(2) Color developing → bleaching → fixing → washing → stabilizing
(3) Color developing → bleaching → fixing → stabilizing
(4) Color developing → bleaching → fixing → first stabilizing → second stabilizing
(5) Color developing → bleaching → bleach-fixing → washing
(6) Color developing → bleaching → bleach-fixing → washing → stabilizing
(7) Color developing → bleaching → bleach-fixing → stabilizing
(8) Color developing → bleaching → bleach-fixing → first stabilizing → second stabilizing

Among these steps, preferred are (3), (4), (6), (7) and (8), particularly preferably (3), (4) and (7), most preferably (3).

In the fixing solution and the bleach-fixing solution according to the present invention, a so-called fixing agent is indispensable.

As the fixing agent, there may be included compounds which can form a complex salt of an aqueous solution by reacting with silver halide, for example, thiosulfates such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate, thiocyanates such as potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate, or thiourea and thioether, preferably thiosulfates and thiocyanates. Further, for practicing the present invention, it is a preferred embodiment that 50 % or less, preferably 20 % or less of total cations in the fixing solution or the bleach-fixing solution are ammonium ions similarly as in the bleaching solution, whereby a slight effect on antistaining can be obtained.

Further, in the fixing solution and the bleach-fixing solution, other than these fixing agents, pH buffering agents comprising sulfites such as ammonium sulfite, potassium sulfite, ammonium bisulfite, potassium bisulfite, sodium bisulfite, ammonium metabisulfite, potassium metabisulfite and sodium metabisulfite, boric acid, and various salts such as borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide can be contained singly or in combination of two or more kinds.

Further, a large amount of rehalogenating agents such as an alkali halide or an ammonium halide, for example, potassium bromide, sodium bromide, sodium chloride and ammonium bromide may be desirably contained. In addition, pH buffering agents such as borate, oxalate, acetate, carbonate and phosphate, and those generally known as additives in a fixing solution and a bleach-fixing solution such as alkylamines and polyethylene oxides can be added suitably.

The above fixing agent is used as a fixing agent in an amount of 0.1 mole or more, preferably in the range of 0.3 mole to 4 mole, particularly preferably in the range of 0.5 mole to 3.0 mole, most preferably in the range of 0.6 mole to 2.0 mole per liter of a processing solution for obtaining the effect of the present invention.

In the present invention, for enhancing activity of the bleaching solution or the bleach-fixing solution, air or oxygen may be blown into a processing bath or a tank for storing a processing replenishing solution, if desired, or an appropriate oxidizing agent such as hydrogen peroxide, bromate and persulfate may be added suitably.

When the method of the present invention is practiced, silver may be recovered from the fixing solution or the bleach-fixing solution according to a known method. For example, there may be effectively utilized the electrolysis method (disclosed in French Patent No. 2,299,667), the precipitation method (disclosed in

Japanese Unexamined Patent Publication No. 73037/1977 and West German Patent No. 2,331,220), the ion exchange method (disclosed in Japanese Unexamined Patent Publication No. 17114/1976 and West German Patent No. 2,548,237) and the metal substitution method (disclosed in U.K. Patent No. 1,353,805).

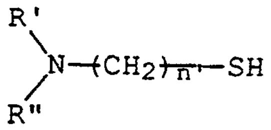
As the silver recovery, an in-line silver recovery from a tank solution is particularly preferred since rapid processing suitability is further improved, but silver may be recovered from an overflow waste liquor and then used again.

When the replenishing amount of the fixing solution and the bleach-fixing solution according to the present invention is 800 ml or less per 1 m^2 of a light-sensitive material, the effect of the present invention can be exhibited more favorably. Particularly, when the amount is preferably 20 ml to 650 ml, particularly preferably 30 ml to 400 ml per 1 m^2 of a light-sensitive material, good results can be obtained.

Further, when an iodide (ammonium iodide, potassium iodide, sodium iodide and lithium iodide) is contained in an amount of 0.1 g/ℓ to 10 g/ℓ in the fixing solution and the bleach-fixing solution according to the present invention, the effect of the present invention can be further enhanced.

When its amount is preferably 0.3 g/ℓ to 5 g/ℓ, particularly preferably 0.5 g/ℓ to 3 g/ℓ, most preferably 0.8 g/ℓ to 2 g/ℓ, good results can be obtained.

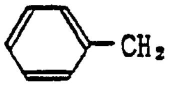
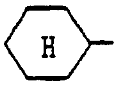
When a compound represented by the following formula (FA) or a compound among the following group of compounds (FB) is added in the fixing solution and the bleach-fixing solution according to the present invention, not only the effect of the present invention can be exhibited more favorably, but also another effect that sludge generated when a small quantity of a light-sensitive material is processed over a long period of time by using the fixing solution and the bleach-fixing solution is extremely small can be obtained additionally, whereby the above compounds are used more preferably in the present invention.

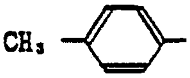
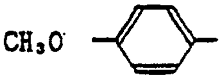
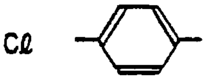
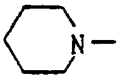
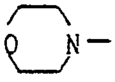
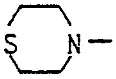
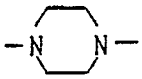
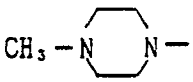


(FA)

wherein R' and R" each represent a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or a nitrogen-containing hetero ring; and n' represents 2 or 3.

Specific exemplary compounds represented by the formula (FA) are shown below.

No.	R′	R″	n′
FA-1	iso—C_3H_7—	H	2
FA-2	n—C_4H_9—	H	2
FA-3	iso—C_4H_9—	H	2
FA-4	sec—C_4H_9—	H	2
FA-5	ter—C_4H_9—	H	2
FA-6	CH=CHCH$_2$—	H	2
FA-7	n—C_6H_{13}—	H	2
FA-8	n—C_8H_{17}—	H	2
FA-9	n—$C_{10}H_{21}$—	H	2
FA-10		H	2
FA-11		H	2
FA-12	C_2H_5—	C_2H_5—	2
FA-13	n—C_3H_7—	n—C_3H_7—	2
FA-14	iso—C_3H_7—	iso—C_3H_7—	2
FA-15	n—C_4H_9—	n—C_4H_9	2
FA-16	iso—C_4H_9	iso—C_4H_9—	2
FA-17	sec—C_4H_9	sec—C_4H_9—	2
FA-18	n—C_5H_{11}—	n—C_5H_{11}—	2
FA-19	iso—C_5H_{11}—	iso—C_5H_{11}—	2
FA-20	$CH_2=CH-CH_2$—	$CH_2=CHCH_2$—	2
FA-21	CH_3—	CH_3—	2

No.	R′	R″	n′
FA-22	$HOCH_2CH_2-$	H—	2
FA-23	$HOCH_2CH_2-$	CH_3-	2
FA-24		H—	2
FA-25		H—	2
FA-26		H—	2
FA-27	C_2H_5-	CH_3-	2
FA-28	C_2H_5-	C_3H_7-	2
FA-29	H	H—	2
FA-30	$CH_2=CH-CH_2-$	C_2H_5-	2
FA-31			2
FA-32			2
FA-33			2
FA-34			2
FA-35			2
FA-36			2
FA-37	C_2H_5-	C_2H_5-	3
FA-38	$HSCH_2CH_2-$	$HSCH_2CH_2-$	2
FA-39	$HSCH_2CH_2-$	$HOOC-CH_2-$	2

These compounds represented by the formula (FA) can be synthesized according to a general method as disclosed in U.S. Patents No. 3,335,161 and No. 3,260,718.

Group of compounds (FB)

FB-1	Thiourea
FB-2	Ammonium iodide
FB-3	Potassium iodide
FB-4	Ammonium thiocyanate
FB-5	Potassium thiocyanate
FB-6	Sodium thiocyanate
FB-7	Thiocyano catechol

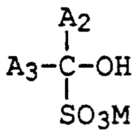
These compounds represented by the above formula (FA) and the compounds of the group of compounds (FB) may be used singly or in combination of two or more kinds, respectively. For example, as a preferred example, there may be mentioned combinations of thiourea, ammonium thiocyanate and ammonium iodide, thiourea and ammonium thiocyanate, (FA-12) and thiourea, (FA-12) and ammonium thiocyanate, (FA-12) and ammonium iodide, (FA-12) and (FA-32), and (FA-12) and (FA-38). Among these, particularly preferred is a combination of thiourea (FB-1) and ammonium thiocyanate (FB-4).

For obtaining good results, the amounts of the compounds represented by the formula (FA) and the compounds of the group of compounds (FB) to be added are each in the range of 0.1 g to 300 g, particularly in the range of 0.2 to 200 g, particularly preferably in the range of 0.5 to 150 g per liter of a processing solution.

In the fixing solution and the bleach-fixing solution according to the present invention, from the point of the effect of the present invention, a sulfite adduct is preferably used.

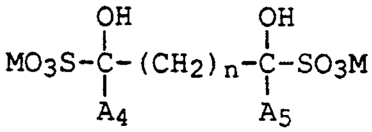
As a compound which forms a stable sulfite adduct with the above sulfite ions, there may be mentioned, for example, a compound having an aldehyde group, a compound containing cyclic hemiacetal, a compound having α-dicarbonyl group and a compound having a nitrile group, but compounds represented by the formulae (A-I) and (A-II) are particularly preferably used.

Preferred specific examples other than the compounds represented by the formulae (A-I) and (A-II) are shown below.



$$A_3-\underset{SO_3M}{\overset{A_2}{\mathrm{C}}}-OH$$

(A-I)



$$MO_3S-\underset{A_4}{\overset{OH}{\mathrm{C}}}-(CH_2)_n-\underset{A_5}{\overset{OH}{\mathrm{C}}}-SO_3M$$

(A-II)

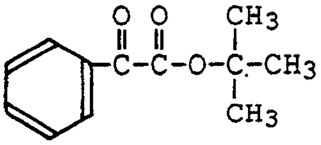
A_2, A_3, A_4 and A_5 each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a formyl group, an acyl group or an alkenyl group. The alkyl group having 1 to 6 carbon atoms may include those which are straight or branched, for example, a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, an n-pentyl group, an iso-pentyl group, a hexyl group and an isohexyl group, which may be substituted. As the substituent group, there may be included specifically a formyl group (e.g. each group of formylmethyl and 2-formylethyl), an amino group (e.g. each group of aminomethyl and aminoethyl), a hydroxyl group (e.g. each group of hydroxymethyl, 2-hydroxyethyl and 2-hydroxypropyl), an alkoxy group (e.g. each group of methoxy and ethoxy) and a halogen atom (e.g. each group of chloromethyl, trichloromethyl and dibromomethyl).

The alkenyl group may be substituted or unsubstituted. The unsubstituted alkenyl group may include each group of vinyl and 2-propenyl, and the substituted one may include, for example, each group of 1,2-dichloro-2-carboxyvinyl and 2-phenylvinyl.

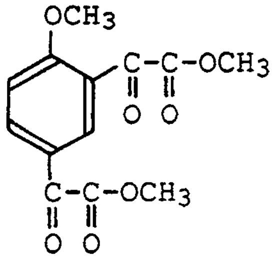
In the following, specific examples of the compound which forms a stable sulfite adduct with the above sulfite ions are shown, but the present invention is not limited to these.

(Exemplary compounds)

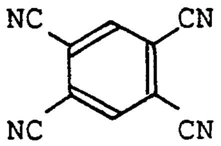
AO-1



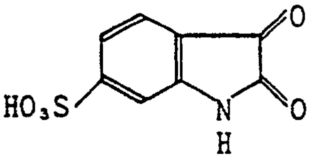
AO-2



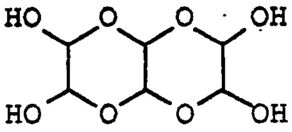
AO-3



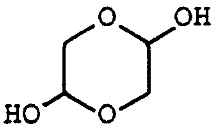
AO-4



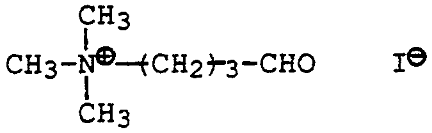
AO-5



AO-6



AO-7



$$CH_3-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-(CH_2)_3-CHO \qquad I^{\ominus}$$

AO-11	Sodium bisulfite formaldehyde
AO-12	Sodium bisulfite acetaldehyde
AO-13	Sodium bisulfite propionaldehyde
AO-14	Sodium bisulfite butyraldehyde
AO-21	Sodium bisulfite succinaldehyde
AO-22	Sodium bisbisulfite glutaraldehyde
AO-23	Sodium bisbisulfite β-methylglutaraldehyde
AO-24	Sodium bisbisulfite maleic dialdehyde

These sulfite adduct compounds are used preferably in an amount in the range of 0.1 g to 80 g, more preferably in the range of 0.5 g to 40 g per liter of a processing solution.

The processing time by the bleaching solution and a processing solution having fixing ability (the fixing solution or the bleach-fixing solution) according to the present invention is preferably 3 minutes and 45 seconds or shorter in total, and when the total processing time is preferably 20 seconds to 3 minutes and 20 seconds, more preferably 40 seconds to 3 minutes, particularly preferably in the range of 60 seconds to 2 minutes and 40 seconds, the effect of the present invention can be exhibited favorably.

The bleaching time can be selected as desired from within the range of the total processing time described above, but preferably 1 minute and 30 seconds or shorter, more preferably 10 seconds to 70 seconds, particularly preferably 20 seconds to 55 seconds for obtaining the effect of the present invention. The processing time by the processing solution having fixing ability can be selected as desired, but preferably 3 minutes and 10 seconds or shorter, more preferably in the range of 10 seconds to 2 minutes and 40 seconds, particularly preferably in the range of 20 seconds to 2 minutes and 10 seconds for obtaining the effect of the present invention.

For preventing bleaching fog, it is a preferred embodiment for practicing the present invention that crossover time between a color developing solution tank and a bleaching solution tank is preferably within 10 seconds, particularly preferably within 7 seconds.

In the processing method of the present invention, it is preferred to give compulsory stirring of a solution to the bleaching solution, the fixing solution and the bleach-fixing solution not only for exhibiting the effect of the present invention more favorably, but also from the standpoint of rapid processing suitability.

Here, the compulsory stirring of a solution refers not to diffusional movement of a solution in general but to compulsory stirring by providing a stirring means.

The stirring means may include the following methods.

1. High pressure spray processing method or spraying stirring method
2. Air bubbling processing method
3. Ultrasonic oscillation processing method
4. Vibration processing method

The high pressure spray processing method is a system in which processing is carried out by spraying a processing solution directly on a light-sensitive material in a processing solution from a spray nozzle by applying a pressure of a discharge pressure of 0.1 kg/cm^2 or higher, and the spraying stirring method is a system in which processing is carried out by spraying a processing solution directly on a light-sensitive material in a processing solution from a nozzle by applying a pressure of a discharge pressure of 0.1 kg/cm^2 or higher. As the pressure source, a pressure pump and a solution-charging pump are generally used. As the pressure pump, there may be mentioned a plunger pump, a gear pump, a magnet pump and a cascade pump, and for example, Model 15-LPM, Model 10-BFM, Model 20-BFM and Model 25-BFM pumps, all trade names, manufactured by Maruyama Seisakusho K.K. have been known as examples thereof.

As the solution-charging pump, there may be mentioned, for example, Model MD-30, Model MO-56, Model MDH-25 and Model MDK-32 pumps, all trade names, manufactured by Iwaki K.K.

The nozzle and the spray nozzle may be of straight advancing type, sector type, round type, whole surface type or round ring type, and those having a strong impact force and giving small vibrations to a light-sensitive material to be processed are effective. The impact force of the spray is determined principally by a flow (ℓ/min) and a spray pressure (kg/cm^2). Accordingly, a pressurizing device which can control a pressure in proportion to a number of spray nozzles so that the effect can be exhibited sufficiently is required. The most preferred pressure is 0.3 to 10 kg/cm^2, and if the pressure is less than 0.3 kg/cm^2, the effect cannot be obtained, and on the other hand, if the pressure is too high, a light-sensitive material is damaged or broken in some cases.

Next, the air bubbling processing method is a method in which a sparger is provided at the bottom of a lower conveying roller of a processing solution tank, air or inert gas is charged into the sparger, a light-sensitive material is vibrated by air bubbles discharged from its opening, and further, a processing solution is brought in contact effectively with a front surface, a back surface and a side surface of a light-sensitive material.

As a material of the sparger, materials having a resistance to corrosion such as rigid vinyl chloride, a stainless steel coated with polyethylene and a sintered metal are suitable, and perforation is carried out to obtain such a perforated diameter that air bubbles discharged have a size of 2 mm to 30 mm, preferably 5 mm to 15 mm, whereby a better effect can be obtained. As a means for charging air, there may be included an air compressor, for example, Babycon (0.4 KW, BU7TL) (trade name) manufactured by Hitachi Ltd. and an air pump, for example, an air pump (Model Ap220, trade name) manufactured by Iwaki K.K. The amount of air is required to be 2 ℓ/min to 30 ℓ/min, preferably 5 ℓ/min to 20 ℓ/min per conveying rack of an automatic processor, whereby more preferred results can be obtained. Depending on a size of a processing solution tank and a quantity of a light-sensitive material, the amount of air or inert gas should be controlled, but air or inert gas is preferably charged in such an amount that a vibration width of a light-sensitive material caused by air bubbles becomes 0.2 mm to 20 mm.

The ultrasonic oscillation processing method is a method in which an ultrasonic oscillation device is provided in a space at a bottom portion or a side wall within a processing solution tank of an automatic processor, and ultrasonic waves are irradiated to a light-sensitive material to enhance development accelerating efficiency. As the ultrasonic oscillation device, there may be used, for example, a magnetostrictive type nickel oscillator (horn type) and a magnetostrictive type barium titanate oscillator (holder type) manufactured by Choonpa Kogyo K.K.

A frequency of an oscillator of the ultrasonic oscillation device to be used is preferably 5 to 1,000 KHz, particularly preferably 10 to 50 KHz in the points of the effect of the present invention and damage to machine parts of an automatic processor. As an irradiation method of ultrasonic waves to a light-sensitive material, there may be included a method in which ultrasonic waves are irradiated directly or indirectly through a reflecting plate to a light-sensitive material. However, since ultrasonic waves are damped in proportion to an irradiating distance, a direct irradiation is more preferred. The irradiation time may be at least 1 second. When a partial irradiation is effected, it may be effected at any of a primary stage, an intermediate stage or a latter stage of processing steps.

Further, the vibration processing method is a method in which a light-sensitive material is vibrated between an upper roller and a lower roller in a processing solution tank of an automatic processor to carry out immersion processing effectively. As a vibrator which is a vibration source, there may be generally used, for example, Model V-2B and Model V-4B both trade names manufactured by Shinko Denki K.K. The vibrator is fixed to the upper portion of a immersion processing tank of an automatic processor and set so that the vibrator strikes against the back side of a light-sensitive material. The vibration number of the vibrator is preferably 100 to 10,000 times/min, most preferably in the range of 500 to 6,000 times/min. A vibrational amplitude of a light-sensitive material to be processed is 0.2 mm to 30 mm, preferably 1 mm to 20 mm. If the amplitude is lower than 0.2 mm, no effect can be exhibited, and on the other hand, if it is too great, a light-sensitive material may be damaged in some cases. The number of vibrators to be set may be different depending on a size of an automatic processor. When a processing tank comprises a plural number of tanks, at least one vibrator is set per one processing tank for obtaining preferred effect.

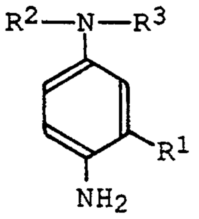
In the present invention, the processing time of a light-sensitive silver halide color photographic material by using a color developing solution is preferably 210 seconds or shorter and 10 seconds or longer.

In the method for processing a light-sensitive silver halide color photographic material of the present invention, the color developing solution is a color developing solution containing an aromatic primary amine type color developing agent preferably in an amount of 5.0×10^{-3} mole or more, more preferably 1.0×10^{-2} mole or more, particularly preferably 1.2×10^{-2} to 2×10^{-1} mole per liter of the processing solution.

The color developing agent of the color developing solution which can be preferably used in the present invention is described below.

The aromatic primary amine type color developing agent used in the preferred color developing solution as described above may include those known to the art which have been used widely in various color photographic processings. These developing agents may include aminophenol type and p-phenylenediamine type derivatives. These compounds are generally used in the form of a salt, for example, in the form of a chloride or a sulfate since they are stabler than those under a free state. As the aminophenol type developing agent, there may be mentioned, for example, o-aminophenol, p-aminophenol, 5-amino-2-oxy-toluene, 2-amino-3-oxy-toluene and 2-oxy-3-amino-1,4-dimethyl-benzene.

In the present invention, for exhibiting the effect more favorably and for improving crystal precipitation property to an inner wall of a color developing tank of an automatic processor, the aromatic primary amine color developing agent particularly useful in the present invention is an aromatic primary amine color developing agent having an amino group containing at least one water-soluble group, particularly preferably a compound represented by the following formula (E).



(E)

In the above formula, R^1 represents a hydrogen atom, a halogen atom or an alkyl group, and said alkyl group represents a straight or branched alkyl group having 1 to 5 carbon atoms, which may have a substituent group.

R^2 and R^3 each represent a hydrogen atom, or an alkyl group or an aryl group, and these groups may have a substituent group. At least one of R^2 and R^3 is an alkyl group substituted with a water-soluble group such as a hydroxyl group, a carboxylic acid group, a sulfonic acid group, an amino group and a sulfonamide group, or

$$-\!\!\left[\left(CH_2\right)_q O\right]_p R_4 .$$

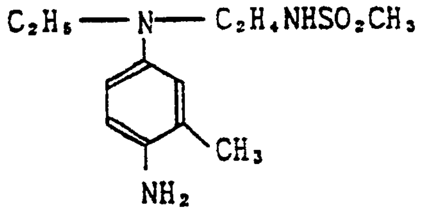
The alkyl group may further have a substituent group.

R^4 represents a hydrogen atom or an alkyl group, the alkyl group represents a straight or branched alkyl group having 1 to 5 carbon atoms, and p and q each represent an integer of 1 to 5.

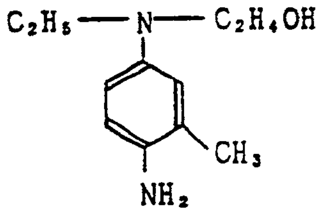
In the following, compounds represented by the above formula (E) are shown, but the present invention is not limited to these.

(Exemplary compounds)

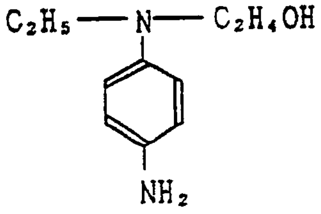
(E - 1)


C₂H₅
N
C₂H₄NHSO₂CH₃
CH₃
NH₂

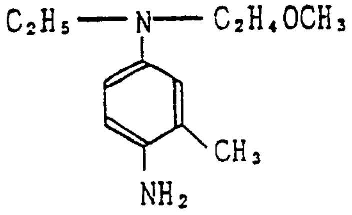
(E - 2)


C₂H₅
N
C₂H₄OH
CH₃
NH₂

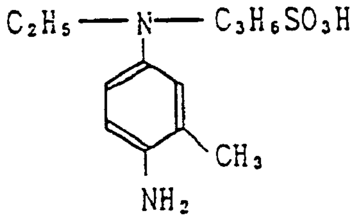
(E - 3)


C₂H₅
N
C₂H₄OH
NH₂

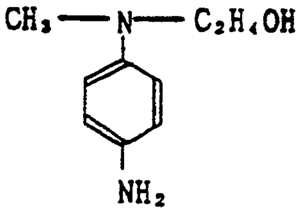
(E - 4)


C₂H₅
N
C₂H₄OCH₃
CH₃
NH₂

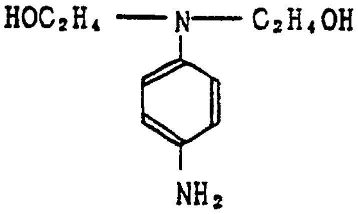
(E - 5)


C₂H₅
N
C₃H₆SO₃H
CH₃
NH₂

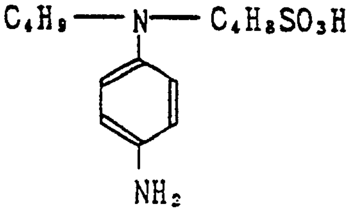
(E - 6)



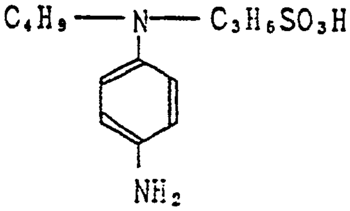
(E - 7)



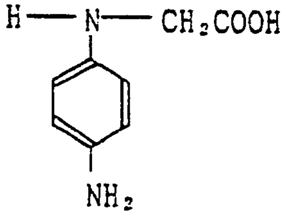
(E - 8)



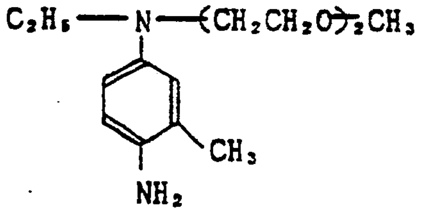
(E - 9)



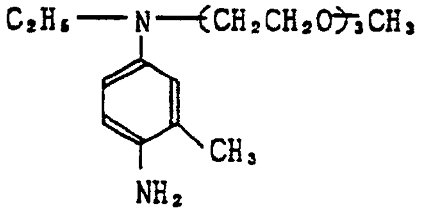
(E - 10)



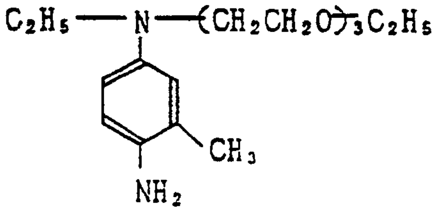
(E - 11)



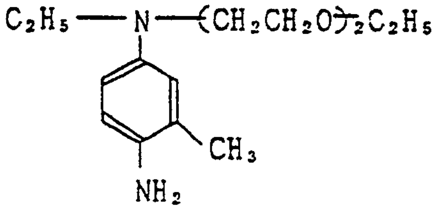
(E - 12)



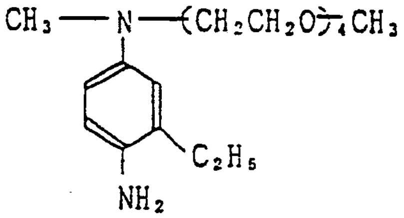
(E - 13)



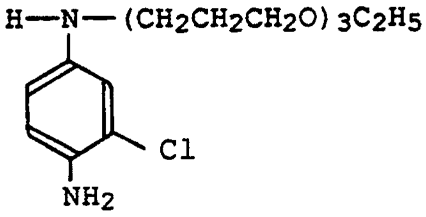
(E - 14)



(E - 15)



(E - 16)



These p-phenylenediamine derivatives represented by the formula (E) can be used as a salt of an organic acid or an inorganic acid, and, for example, hydrochlorides, sulfates, phosphates, p-toluenesulfonates, sulfites, oxalates and benzenedisulfonates can be used.

In the present invention, among the p-phenylenediamine derivatives represented by the above formula (E), E-1 and E-2 are used most preferably for exhibiting the effect of the present invention remarkably.

As a preservative used in the color developing solution to be used in the present invention, there may be mentioned sulfites, and the sulfites may include sodium sulfite, sodium hydrogen sulfite, potassium sulfite and potassium hydrogen sulfite. When the silver halide is substantially a silver chloride emulsion, the sulfite is used in an amount of 1.0×10^{-2} mole/ℓ or less, preferably 5.0×10^{-3} mole/ℓ or less, particularly preferably 0. When the silver halide is a silver iodobromide emulsion, the sulfite may be used preferably in an amount in the range of 0.1 to 40 g/ℓ, more preferably in the range of 0.5 to 10 g/ℓ.

As a preservative other than the sulfites, there may be preferably used, as organic preservatives, hydroxylamine, hydroxylamine derivatives disclosed in Japanese Unexamined Patent Publications No. 146043/1988, No. 146042/1988, No. 146041/1988, No. 146040/1988, No. 135938/1988 and No. 118748/1988, and hydroxamic acids, hydrazines, hydrazides, phenols, α-hydroxyketones, α-aminoketones, saccharides, monoamines, diamines, quaternary ammonium salts, nitroxy radicals, alcohols, oximes, diamide compounds and fused ring type amines disclosed in Japanese Unexamined Patent Publication No. 62639/1989.

Particularly, when the silver halide is silver chloride having a high concentration, organic preservatives other than hydroxylamine, particularly hydroxylamine derivatives substituted with alkyl and hydrazines are preferably used.

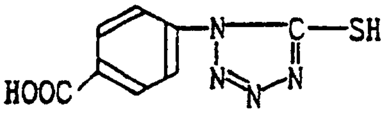
Further, as a development inhibitor preferably used in the above color developing solution, there may be mentioned halides such as sodium chloride, potassium chloride, sodium bromide, potassium bromide, sodium iodide and potassium iodide and further organic inhibitors. Their amounts to be added are preferably in the range of 0.005 to 30 g/ℓ, more preferably in the range of 0.01 to 20 g/ℓ.

As the above organic inhibitor preferably used when the present invention is practiced, there may be mentioned nitrogen-containing heterocyclic compounds, compounds containing a mercapto group, aromatic compounds, onium compounds and compounds having an iodine atom as a substituent group, and specific examples of them are the following exemplary compounds.

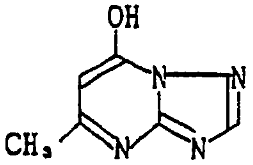
However, the compounds which can be used are not limited to the following compounds.

(Exemplary compounds)

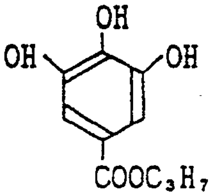
(Z—1)



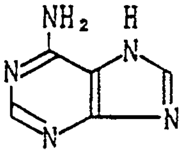
(Z—2)



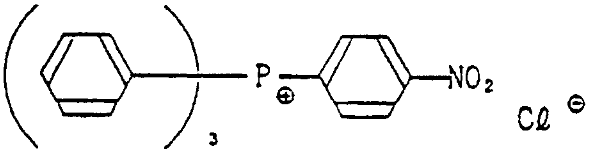
(Z—3)



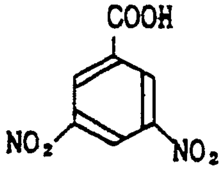
(Z—4)



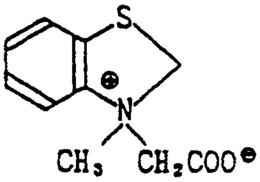
(Z—5)



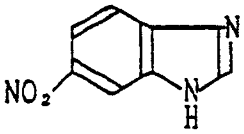
(Z—6)



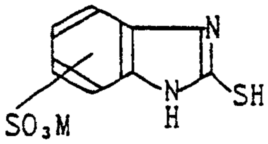
(Z—7)



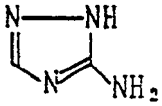
(Z—8)



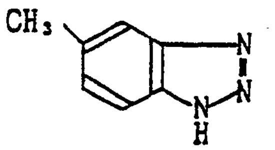
(Z—9)



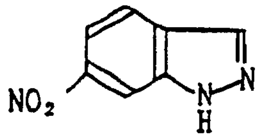
(Z—10)



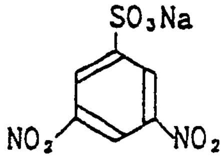
(Z—11)



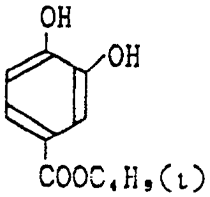
(Z—12)



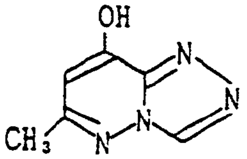
(Z—13)



(Z—14)



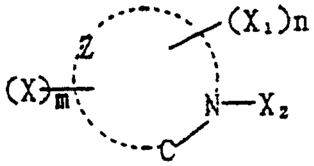
(Z—15)



Among the above organic inhibitors, preferred are compounds represented by the following formulae (R-I), (R-II) and (R-III).

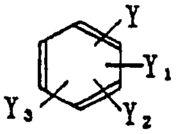
The compound represented by the following formula (R-I) is more preferably a compound represented by the formula (R-IV) or (R-V), most preferably compounds represented by the formulae (R-VI) to (R-XI).

On the other hand, the compound represented by the following formula (R-II) is most preferably a compound represented by the formula (R-XII) or (R-XIII).



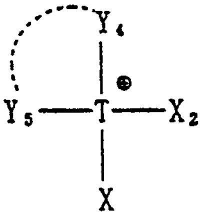
(R-I)

wherein X and X_1 each represent a halogen atom, a mercapto group, an oxycarbonyl group, an alkyl group, an aryl group, an amino group, a hydroxyl group, a nitro group, a carboxyl group and a sulfo group; X_2 represents a hydrogen atom, an alkyl group, an aryl group or a double bond for forming a ring; Z is an atomic group necessary for forming a ring comprising a carbon atom, a nitrogen atom and a sulfur atom; n and m each represent 0, 1 or 2; and when n and m are 2, each X and X_1 may be the same or different.



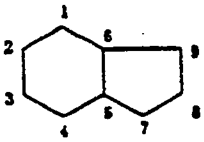
(R-II)

wherein Y, Y_1, Y_2 and Y_3 each represent a hydrogen atom, a halogen atom, an alkyl group, an amino group, a hydroxyl group, a nitro group, a carboxyl group, an oxycarbonyl group, a sulfo group and a sulfonyl group.



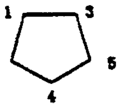
(R-III)

wherein T represents a nitrogen atom or a phosphor atom; X_2 and X_3 each represent a hydrogen atom, an alkyl group, an aryl group or a halogen atom; Y_4 and Y_5 each represent an alkyl group or an aryl group; and Y_4 and Y_5 may be closed to form a hetero ring.



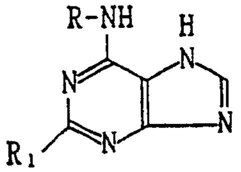
(R-IV)

Compound in which 2 to 5 carbon atoms at the positions of 1 to 9 are substituted with nitrogen atoms, and a derivative thereof

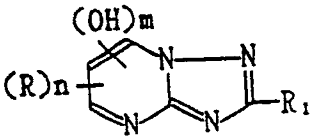


(R-V)

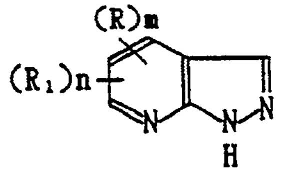
Compound in which 2 to 4 carbon atoms at the positions of 1 to 5 are substituted with nitrogen atoms, and a derivative thereof



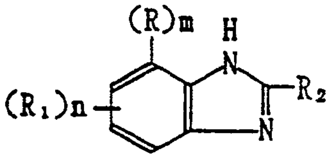
(R-VI)



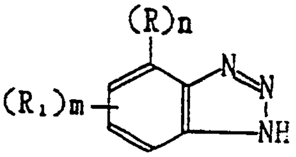
(R-VII)



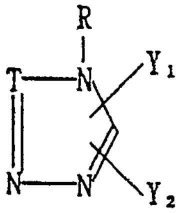
(R-VIII)



(R-IX)

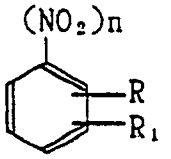


(R-X)

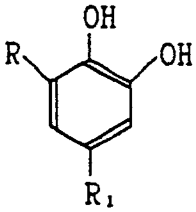


(R-XI)

(T is CR_1 or N)



(R-XII)



(R-XIII)

In the above formulae (R-IV) to (R-XIII), R, R_1, R_2, Y_1 and Y_2 have the same meanings of Y, Y_1, Y_2 and Y_3 in the description of the above formula (R-II), respectively. m and n have the same meanings of those in the formula (R-I).

By using said organic inhibitor in combination with the above inorganic inhibitor, the effect of the present invention can be exhibited more remarkably.

The organic inhibitor in the present invention has been described above, and further specific examples thereof may include (Z-1) to (Z-3), (Z-6), (Z-8), (Z-13), (Z-15) to (Z-17), (Z-19), (Z-22) to (Z-25), (Z-29), (Z-31) to (Z-38), (Z-40), (Z-41), (Z-43) to (Z-64) and (Z-66) to (Z-73) described on pp. 101 to 113 of Japanese Unexamined Patent Publication No. 170955/1987.

In the color developing solution to be used in the present invention, various components generally added, for example, alkali agents such as sodium hydroxide and sodium carbonate, alkali metal thiocyanate, alkali metal halides, benzyl alcohol, a water softener, a thickener and a developing accelerator can be further contained as desired.

Other additives added in the above color developing solution may include an antistaining agent, an antisludging agent, a preservative, an interlayer effect accelerator and a chelating agent.

The color developing solution of the present invention is used preferably at a pH of 9 or more, particularly preferably at a pH of 9 to 13.

For exhibiting the effect which accomplishes the objects of the present invention more favorably, the color developing solution is employed preferably at a temperature of 30 °C or higher, particularly preferably in the range of 33 °C to 60 °C.

Next, the stabilizing solution to be used in the present invention is described. The stabilizing solution to be used in the present invention can be applied to a stabilizing solution used in a stabilizing processing which is the final processing step of a light-sensitive silver halide color photographic material. Further, the present invention can be also applied to the case where a light-sensitive silver halide color photographic material is processed by a processing solution having fixing ability, for example, a fixing solution or a bleach-fixing solution, followed by stabilizing processing substantially without washing. The light-sensitive silver halide color photographic material to be processed is not particularly limited and may include negative films, printing papers and color copies, and can be processed by using the stabilizing solution of the present invention.

The replenishing amount of the stabilizing solution of the present invention is preferably 1- to 80-fold of the amount brought in from the previous bath per unit area of a color photographic material to be processed, but in the present invention, a stabilizing processing tank is preferably constituted so that the concentration of the components of the previous bath (the bleach-fixing solution or the fixing solution) in the stabilizing solution becomes 1/100 or less, preferably 1/100 to 1/100000, more preferably 1/200 to 1/50000 in the ultimate stabilizing solution tank in the points of low pollution and solution storability.

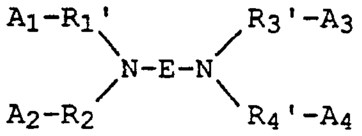
The stabilizing processing tank may be constituted of plural tanks, and said plural tanks are preferably 2 tanks to 6 tanks in the present invention.

In the present invention, when the stabilizing processing tank comprises 2 tanks or more, a countercurrent system (a system in which a solution is supplied to a latter bath and then a solution is overflown from a previous bath) is employed particularly preferably in the point of the effect of the present invention, particularly in the points of low pollution and improvement of image storage.

The amount to be brought in varies depending on a kind of a light-sensitive material, conveying speed and a conveying system of an automatic processor, and a squeeze system of a light-sensitive material surface, but in the case of a light-sensitive color material, the amount to be brought in is generally 50 ml/m^2 to 150 ml/m^2. The replenishing amount which can exhibit the effect of the present invention more markedly relative to said amount to be brought in is in the range of 50 ml/m^2 to 4.0 ℓ/m^2, particularly in the range of 100 ml/m^2 to 1,500 ml/m^2.

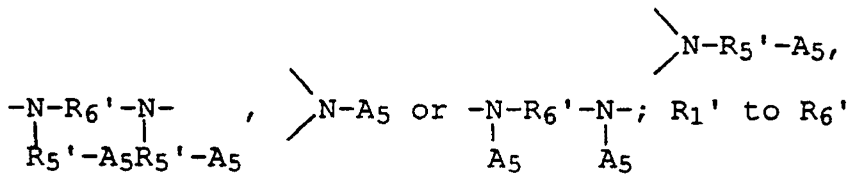
The processing with the stabilizing solution is carried out at a processing temperature of 15 to 60 °C, preferably in the range of 20 to 45 °C.

In the stabilizing solution of the present invention, chelating agents represented by the following formulae (CH-I) to (CH-III) are preferably contained.

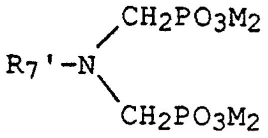


(CH-1)

wherein E represents an alkylene group, a cycloalkylene group, a phenylene group, -R$_5$'-O-R$_5$'-, -R$_5$'-O-R$_5$'-O-R$_5$'-or -R$_5$'-Z-R$_5$'- where Z represents

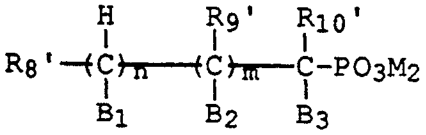


$-\underset{R_5'-A_5}{N}-R_6'-\underset{R_5'-A_5}{N}-$, $>N-A_5$ or $-\underset{A_5}{N}-R_6'-\underset{A_5}{N}-$; $>N-R_5'-A_5$, R$_1$' to R$_6$' each represent an alkylene group; A$_1$ to A$_3$ each represent -COOM or -PO$_3$M$_2$; and A$_4$ and A$_5$ each represent a hydrogen atom, a hydroxyl group, -COOM or -PO$_3$M$_2$ where M represents a hydrogen atom or an alkali metal atom.



(CH-II)

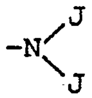
wherein R_7' represents an alkyl group, an aryl group or a nitrogen-containing 6-membered cyclic group; and M represents a hydrogen atom or an alkali metal atom.



$$R_8'-\left(\underset{B_1}{\overset{H}{C}}\right)_n-\left(\underset{B_2}{\overset{R_9'}{C}}\right)_m-\underset{B_3}{\overset{R_{10}'}{C}}-PO_3M_2$$

(CH-III)

wherein R_8', R_9' and R_{10}' each represent a hydrogen atom, a hydroxyl group, -COOM, $-PO_3M_2$ or an alkyl group; B_1, B_2 and B_3 each represent a hydrogen atom, a hydroxyl group, -COOM, $-PO_3M_2$ or

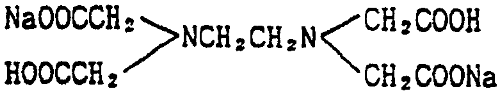


where J represents a hydrogen atom, an alkyl group, $-C_2H_4OH$ or $-PO_3M_2$ where M represents a hydrogen atom or an alkali metal atom; and n and m each represent 0 or 1.

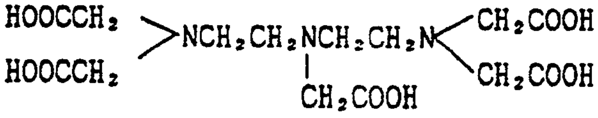
In the following, partial specific examples of the chelating agents represented by the formulae (CH-I), (CH-II) and (CH-III) are shown. The chelating agent to be used in the present invention is not limited to the following specific examples.

(Exemplary chelating agents)

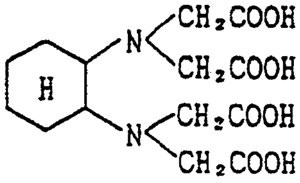
(1)



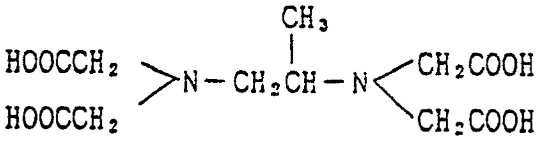
(2)



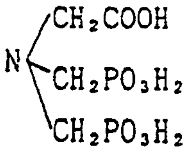
(3)



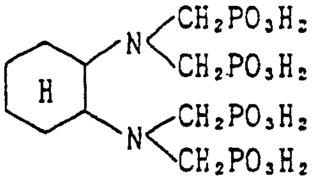
(4)



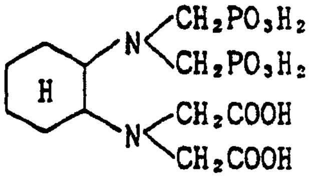
(5)



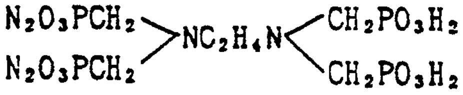
(6)



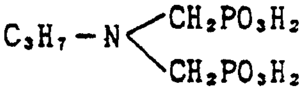
(7)



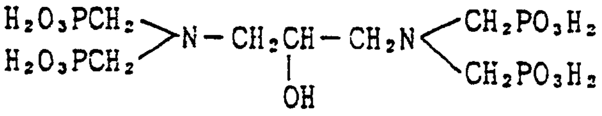
(8)



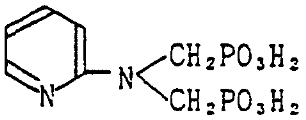
(9)



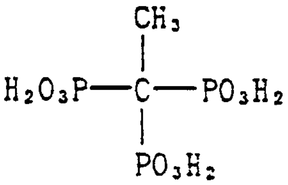
(10)



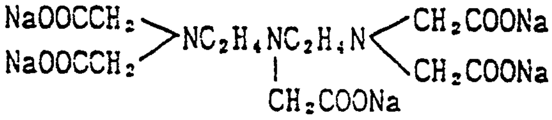
(11)



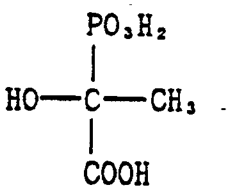
(12)



(13)

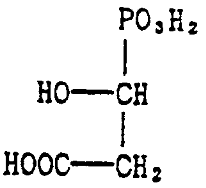


(14)



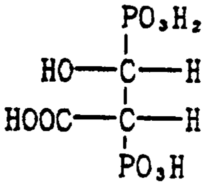
$\mathrm{HO{-}C(PO_3H_2)(CH_3){-}COOH}$

(15)



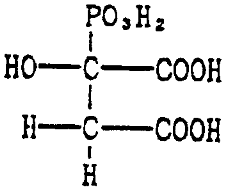
$\mathrm{PO_3H_2{-}CH(OH){-}CH_2{-}COOH}$

(16)



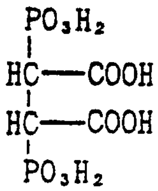
$\mathrm{PO_3H_2{-}C(OH)(H){-}C(COOH)(H){-}PO_3H}$

(17)



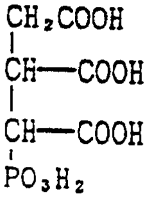
$\mathrm{PO_3H_2{-}C(OH)(COOH){-}C(H)(H){-}COOH}$

(18)



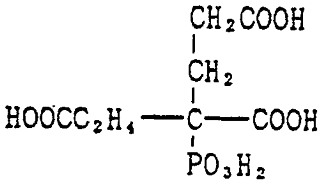
$\mathrm{PO_3H_2{-}HC(COOH){-}HC(COOH){-}PO_3H_2}$

(19)



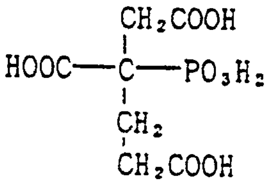
$\mathrm{CH_2COOH{-}CH(COOH){-}CH(COOH){-}PO_3H_2}$

(20)



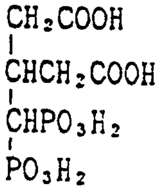
$\mathrm{HOOCC_2H_4{-}C(COOH)(PO_3H_2){-}CH_2{-}CH_2COOH}$

(21)



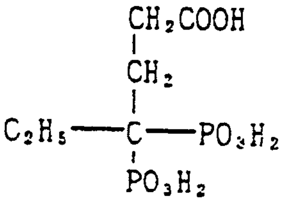
$\mathrm{HOOC{-}C(PO_3H_2)(CH_2COOH){-}CH_2{-}CH_2COOH}$

(22)



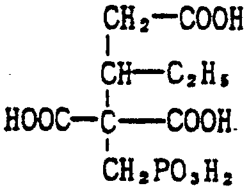
$\mathrm{CH_2COOH{-}CHCH_2COOH{-}CHPO_3H_2{-}PO_3H_2}$

(23)



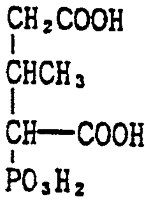
$\mathrm{C_2H_5{-}C(PO_3H_2)(PO_3H_2){-}CH_2{-}CH_2COOH}$

(24)



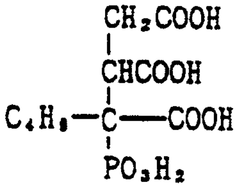
$\mathrm{HOOC{-}C(COOH)(CH_2PO_3H_2){-}CH(C_2H_5){-}CH_2{-}COOH}$

(25)



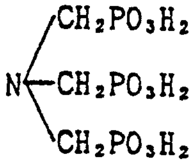
$\mathrm{CH_2COOH{-}CHCH_3{-}CH(COOH){-}PO_3H_2}$

(26)



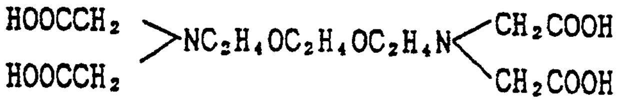
$\mathrm{C_4H_9{-}C(COOH)(PO_3H_2){-}CHCOOH{-}CH_2COOH}$

(27)



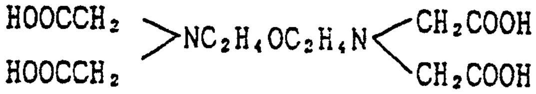
$\mathrm{N(CH_2PO_3H_2)_3}$

(28)



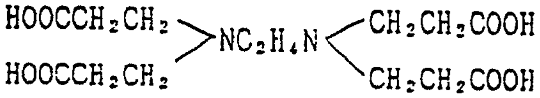
$\mathrm{(HOOCCH_2)_2NC_2H_4OC_2H_4OC_2H_4N(CH_2COOH)_2}$

(29)



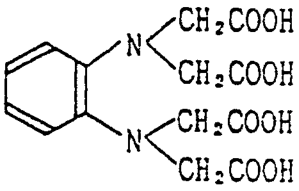
$\mathrm{(HOOCCH_2)_2NC_2H_4OC_2H_4N(CH_2COOH)_2}$

(30)

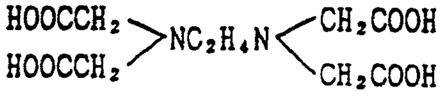


$\mathrm{(HOOCCH_2CH_2)_2NC_2H_4N(CH_2CH_2COOH)_2}$

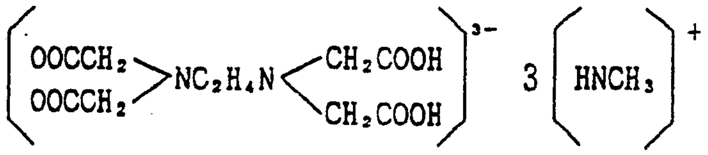
(31)



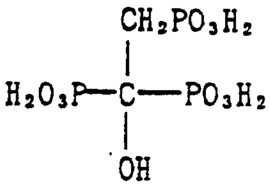
(32)



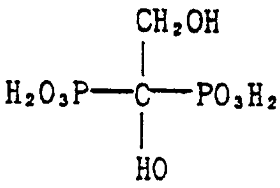
(33)



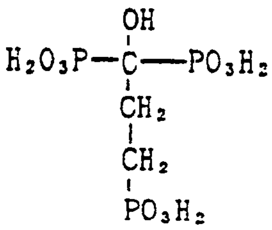
(34)



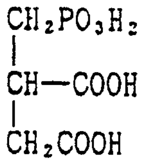
(35)



(36)

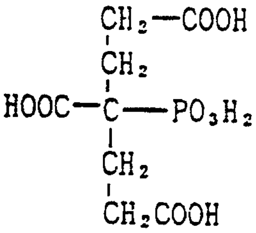


(37)

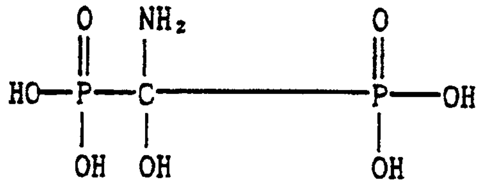


$$\begin{array}{l} CH_2PO_3H_2 \\ | \\ CH-COOH \\ | \\ CH_2COOH \end{array}$$

(38)

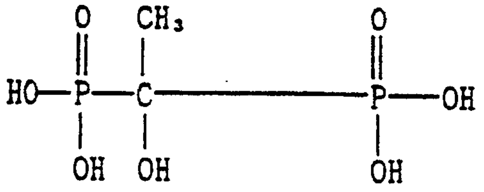


(39)



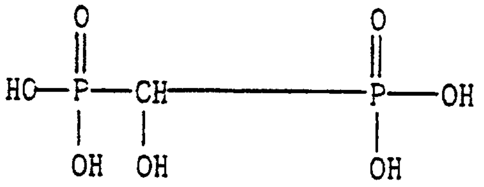
$HO-P(=O)(OH)-C(NH_2)(OH)-P(=O)(OH)-OH$

(40)



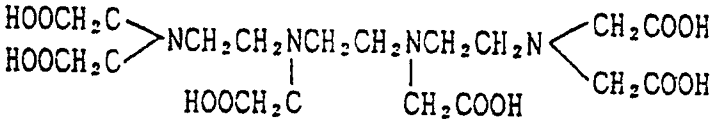
$HO-P(=O)(OH)-C(CH_3)(OH)-P(=O)(OH)-OH$

(41)



$HO-P(=O)(OH)-CH(OH)-P(=O)(OH)-OH$

(42)



$(HOOCH_2C)_2NCH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)_2$

The above chelating agents preferably used in the stabilizing solution are used preferably in an amount of 0.01 to 100 g, more preferably 0.05 to 50 g, particularly preferably 0.1 to 20 g per liter of the stabilizing solution of the present invention.

For the purpose of improving image storability, the stabilizing solution has preferably a pH value in the range of 4.0 to 9.0, more preferably in the range of 5.5 to 9.0, particularly preferably in the range of 6.0 to 8.5.

As a pH controller which can be contained in the stabilizing solution, any alkali agent or acidic agent generally known can be used.

In the stabilizing solution, organic acid salts (salts of citric acid, acetic acid, succinic acid, oxalic acid and benzoic acid), pH controllers (phosphate, borate, hydrochloride and sulfate), surfactants, antiseptic agents and salts of metals such as Bi, Mg, Zn, Ni, Al, Sn, Ti and Zr can be added. These compounds may be added in any desired combination of amounts within the range which is required to maintain a pH value in a stabilizing bath and also exerts bad influence neither on stability of color photographic images during storage nor generation of precipitation. Further, for exhibiting the above effect, Ca and Mg ions may be contained in an amount of 5 ppm or less in the stabilizing solution.

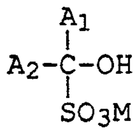
As an antifungal agent preferably used in the stabilizing solution to be used in the present invention, there may be included hydroxybenzoate compounds, phenol type compounds, thiazole type compounds, pyridine type compounds, guanidine type compounds, carbamate type compounds, morpholine type compounds, phosphonium type compounds, quaternary ammonium type compounds, urea type compounds, isoxazole type compounds, propanolamine type compounds, sulfamide type compounds, amino acid type compounds and benztriazole type compounds.

Further, from the standpoint of solution storability, phenol type compounds, thiazole type compounds and benztriazole type compounds are particularly preferred.

Specific examples may include 1,2-benzisothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, 2-octyl-4-iscthiazolin-3-one, 5-chloro-2-methyl-4-isothiazolin-3-one, o-phenylphenol sodium and benztriazole. The amount of the antifungal agents to be added in the stabilizing solution are preferably in the range of 0.001 to 20 g, particularly preferably in the range of 0.005 to 10 g per liter of the stabilizing solution.

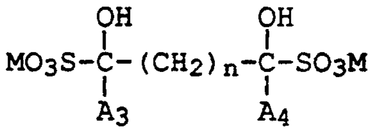
In the stabilizing solution of the present invention, for the purpose of stabilizing dyes, formalin, hexamethylenetetramine, triazine type compounds, N-methylol compounds (dimethylolurea, trimethylolurea, dimethylolguanidine, N-hyroxymethylhydroxyethylamine and trimethylolmelamine) and aliphatic aldehyde can be used in combination. From the standpoint of pollution, the amount of formalin is preferably made 0, which is a preferred embodiment also from the point of solution storability.

In the stabilizing solution to be used in the present invention, sulfite ion-releasing compounds and at least one of compounds represented by the following formulae (SA) and (SB) are preferably contained, whereby solution storability can be further improved without exerting any bad influence on photographic performances.



$$A_2-\underset{SO_3M}{\overset{A_1}{C}}-OH$$

(SA)



$$MO_3S-\underset{A_3}{\overset{OH}{C}}-(CH_2)_n-\underset{A_4}{\overset{OH}{C}}-SO_3M$$

(SB)

In the above formulae, A_1, A_2, A_3 and A_4 each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a formyl group, an acyl group or an alkenyl group. M represents an alkali metal atom (Na, K and Li). n represents an integer of 1 to 5.

The alkyl group having 1 to 6 carbon atoms may include those which are straight or branched, for example, a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an n-pentyl group, an iso-pentyl group, an n-hexyl group and an isohexyl group, which may be substituted. As the substituent group, there may be mentioned specifically a formyl group (e.g. each group of formylmethyl and 2-formylethyl), an amino group (e.g. each group of aminomethyl and aminoethyl), a hydroxyl group (e.g. each group of hydroxymethyl, 2-hydroxyethyl and 2-hydroxypropyl), an alkoxy group (e.g. each group of methoxy and ethoxy) and a halogen atom (e.g. each group of chloromethyl, trichloromethyl and dibromomethyl).

The alkenyl group may be substituted or unsubstituted. The unsubstituted alkenyl group may include each group of vinyl and 2-propenyl, and the substituted one may include, for example, each group of 1,2-dichloro-2-carboxyvinyl and 2-phenylvinyl.

In the following, specific examples of the compounds represented by the above formulae (SA) and (SB) are shown, but the present invention is not limited to these.

(Exemplary compounds)

SA-1	Sodium bisulfite formaldehyde
SA-2	Sodium bisulfite acetaldehyde

SA-3	Sodium bisulfite propionaldehyde
SA-4	Sodium bisulfite butylaldehyde
SB-1	Sodium bisulfite succinaldehyde
SB-2	Sodium bisbisulfite glutaraldehyde
SB-3	Sodium bisbisulfite β-methylglutaraldehyde
SB-4	Sodium bisbisulfite maleic dialdehyde

The compounds represented by the above formulae (SA) and (SB) may be used singly or in combination. The amount to be added is preferably 0.1 to 50 g, more preferably 0.1 to 20 g per liter of the stabilizing solution of the present invention.

The sulfite ion-releasing compound to be used in the present invention may be either an organic compound or an inorganic compound as long as it releases a sulfite ion, but preferably an inorganic salt. Preferred specific examples may include:

SC-1	Sodium sulfite
SC-2	Potassium sulfite
SC-3	Ammonium sulfite
SC-4	Ammonium bisulfite
SC-5	Potassium bisulfite
SC-6	Sodium bisulfite
SC-7	Sodium metabisulfite
SC-8	Potassium metabisulfite
SC-9	Ammonium metabisulfite
SC-10	Hydrosulfite

The amount of the above sulfite ion-releasing compound to be added in a washing-substituting stabilizing solution, a stabilizing solution and a processing solution by which a washing-substituting stabilizing processing and a stabilizing processing can be carried out at the same time is preferably 0.01 to 0.1 mole/ℓ, more preferably 0.02 to 0.1 mole/ℓ.

Further, in the stabilizing solution to be used in the present invention, surfactants represented by the following formulae (I) and (III), triethanolamine and polyvinyl pyrrolidones are preferably contained.

$$R_1\text{-O}\!-\!\left(R_2\text{-O}\right)_m\!-\!X_1 \qquad \text{(I)}$$

wherein R_1 represents a monovalent organic group; R_2 represents an ethylene group or a propylene group; m represents an integer of 4 to 50; and X_1 represents a hydrogen atom, $-SO_3M$ or $-PO_3M_2$ where M represents a hydrogen atom, an alkali metal atom or $-NH_4$.

Specific exemplary compounds may include:

I - 1

$C_{12}H_{25}O(C_2H_4O)_{10}H$

I - 2

$C_8H_{17}O(C_3H_6O)_{15}H$

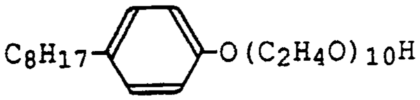
I - 3

$C_9H_{19}O(C_2H_4O)_4SO_3Na$

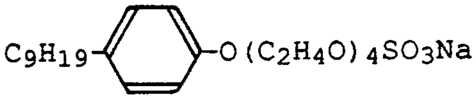
I - 4

$C_{10}H_{21}O(C_2H_4O)_{15}PO_3Na_2$

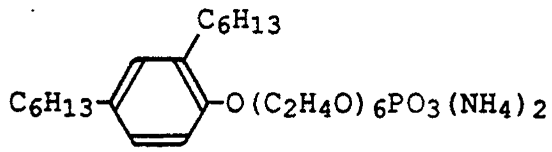
I - 5



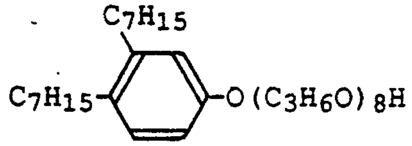
I - 6



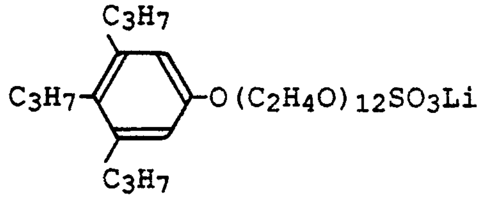
I - 7



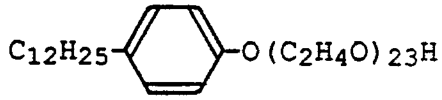
I - 8



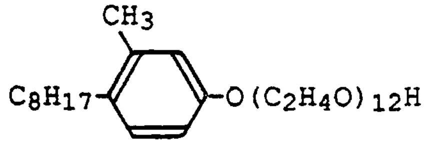
I - 9



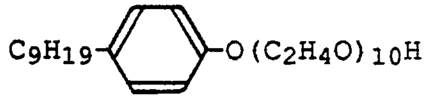
I - 10



I - 11



I - 12



The compounds represented by the above formula (I) can be used in an amount in the range of 0.1 to 40 g, preferably in the range of 0.3 to 20 g per liter of the stabilizing solution of the present invention.

The polyvinyl pyrrolidones to be used in the present invention may preferably have an average molecular weight of 1,000 to 70,000, and their representative specific examples may include the following compounds.

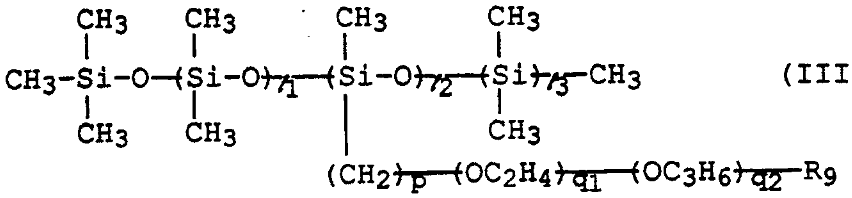
(Exemplary compounds)

(P-1)	Poly-N-vinyl-2-pyrrolidone (see Note 1)
(P-2)	Poly-N-(2-acryloyloxy)ethyl-1-pyrrolidone
(P-3)	Poly-N-glycidyl-2-pyrrolidone
(P-4)	Poly-N-allyl-2-pyrrolidone
(P-5)	Poly-N,N-dimethyl-N-[3(1-pyrrolidonyl)-2-hydroxy]propyl-amine-N'-acryloylimine
(P-6)	Copoly-N-vinyl-2-pyrrolidone/N-acryloylmorpholine (molar ratio: 42:58)
(P-7)	Copoly-N-vinyl-2-pyrrolidone/N-acryloylpiperidine (molar ratio: 35:65)
(P-8)	Poly-N-vinyl-2-pyrrolidone/N-methacryloyl-2-methylimidazole (molar ratio: 55:45)
(P-9)	Copoly-N-(2-acryloyloxy)-ethyl-2-pyrrolidone/diethylamide acrylate (molar ratio: 60:40)

(P-10) Copoly-N-(2-methacryloyloxy)ethyl-2-pyrrolidone/sodium acrylate (molar ratio: 75:25)
(P-11) Copoly-N-(3-acryloyloxy)propyl-2-pyrrolidone/methyl methacrylate (molar ratio: 65:35)
(P-12) Copoly-N,N-dimethyl-N-[3-(1-pyrrolidonyl)-2-hydroxy]-propylamine-N'-acryloylimine/ethyl acrylate (molar ratio: 70:30)
(P-13) Copoly-N-vinyl-2-pyrrolidone/vinyl acetate (molar ratio: 70:30)
(P-14) Copoly-N-vinyl-2-pyrrolidone/methyl acrylate (molar ratio: 70:30)
(P-15) Copoly-N-vinyl-2-pyrrolidone/styrene (molar ratio: 80:20)
(P-16) Copoly-N-vinyl-2-pyrrolidone/acrylamide/N-vinyl-2-methylimidazole (molar ratio: 50:30:20)
(P-17) Copoyl-N-vinyl-2-pyrrolidone/N-(1,1-dimethyl-3-oxo)-butyl-acrylamide (molar ratio: 70:30)
(P-18) Copoly-N-allyl-2-pyrrolidone/vinyl acetate (molar ratio: 64:36)
(P-19) Copoly-N-vinyl-2-pyrrolidone/4-vinylpyridine (molar ratio: 60:40)
(P-20) Copoly-N-vinyl-2-pyrrolidone/ethyl acrylate/monoethanolamine acrylate (molar ratio: 50:45:5)
(P-21) Copoly-N-vinyl-2-pyrrolidone/piperidine piperidinomaleamate (molar ratio: 53:47)
(P-22) Copoly-N-vinyl-pyrrolidone/4-vinylpyridino-N-methyliodide (molar ratio: 42:58)
(P-23) Copoly-N-vinyl pyrrolidone/maleic thiourea half ammonium salt (molar ratio: 60:40)
Note 1: Exemplary compound (P-1) is commercially available under trade names of PVP K-15, PVP K-17, PVP K-30, PVP K-60 and PVP K-90 from General Aniline And Film Corp., and under trade names of Colidon 12, Colidon 17, Colidon 25, Colidon 30, Colidon 90, Lubiskol K-17, Lubiskol K-30 and Lubiskol K-90 from BASF Aktiengesellschaft,Japan.

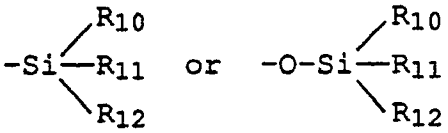
The polymers or copolymers of the present invention can be obtained easily since a part of them are commercially available as described above, and can be synthesized easily according to the method described in "Preparative Methods of Polymer Chemistry" written by W.R. Sorenson and T.W. Campbell published by John Wilery and Sons, Inc. in 1961.

The polymers or copolymers of the present invention may be used singly or in combination of two or more kinds, and their amount to be used are in the range of 0.01 g to 100 g, preferably in the range of 0.05 g to 10 g per liter of the image stabilizing solution. The polymers or copolymers of the present invention may be added in the stabilizing solution, or may be added in a replenishing solution and then replenished in the stabilizing solution, and also these two embodiments may be used in combination.



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-(\overset{CH_3}{\underset{CH_3}{Si}}-O)_{\ell_1}-(\overset{CH_3}{\underset{(CH_2)_p-(OC_2H_4)_{q_1}-(OC_3H_6)_{q_2}-R_9}{Si}}-O)_{\ell_2}-(\overset{CH_3}{\underset{CH_3}{Si}})_{\ell_3}-CH_3 \qquad (III)$$

wherein R_9 represents a hydrogen atom, a hydroxy group, a lower alkyl group, an alkoxy group,

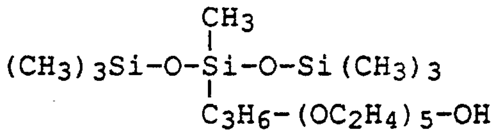


where R_{10}, R_{11} and R_{12} each represent a lower alkyl group (preferably an alkyl group having 1 to 3 carbon atoms such as methyl, ethyl and propyl) and the above R_{10}, R_{11} and R_{12} may be the same or different, respectively; ℓ_1 to ℓ_3 each represent an integer of 0 or 1 to 4; and p, q_1 and q_2 each represent an integer of 1 to 15.

Specific examples of the compound represented by the formula (III) are shown below.

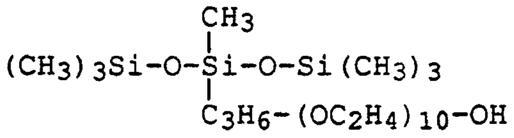
(Water-soluble organic siloxane type compounds)

III - 1



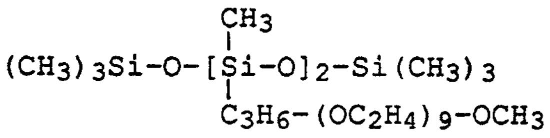
$$(CH_3)_3Si{-}O{-}\overset{\displaystyle CH_3}{\underset{\displaystyle C_3H_6{-}(OC_2H_4)_5{-}OH}{Si}}{-}O{-}Si(CH_3)_3$$

III - 2



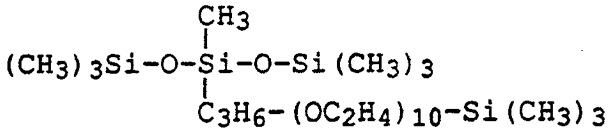
$$(CH_3)_3Si{-}O{-}\overset{\displaystyle CH_3}{\underset{\displaystyle C_3H_6{-}(OC_2H_4)_{10}{-}OH}{Si}}{-}O{-}Si(CH_3)_3$$

III - 3



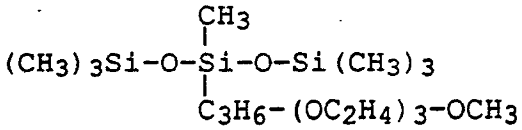
$$(CH_3)_3Si{-}O{-}[\overset{\displaystyle CH_3}{\underset{\displaystyle C_3H_6{-}(OC_2H_4)_9{-}OCH_3}{Si}}{-}O]_2{-}Si(CH_3)_3$$

III - 4



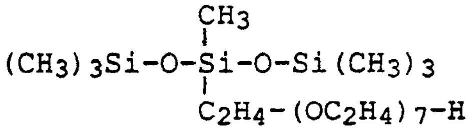
$$\mathrm{(CH_3)_3Si\text{-}O\text{-}\overset{CH_3}{\underset{C_3H_6\text{-}(OC_2H_4)_{10}\text{-}Si(CH_3)_3}{Si}}\text{-}O\text{-}Si(CH_3)_3}$$

III - 5



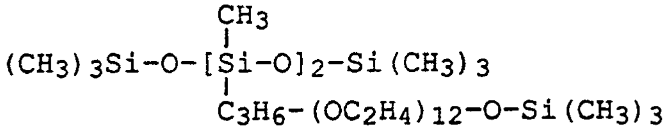
$$\mathrm{(CH_3)_3Si\text{-}O\text{-}\overset{CH_3}{\underset{C_3H_6\text{-}(OC_2H_4)_3\text{-}OCH_3}{Si}}\text{-}O\text{-}Si(CH_3)_3}$$

III - 6



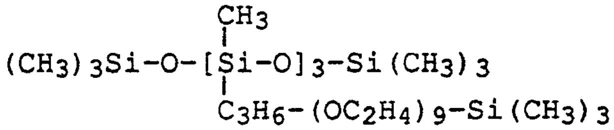
$$\mathrm{(CH_3)_3Si\text{-}O\text{-}\overset{CH_3}{\underset{C_2H_4\text{-}(OC_2H_4)_7\text{-}H}{Si}}\text{-}O\text{-}Si(CH_3)_3}$$

III - 7



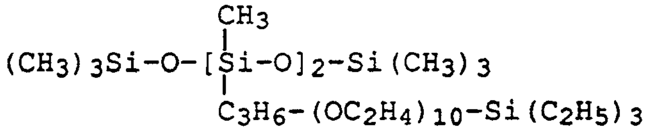
$$\mathrm{(CH_3)_3Si\text{-}O\text{-}[\overset{CH_3}{\underset{C_3H_6\text{-}(OC_2H_4)_{12}\text{-}O\text{-}Si(CH_3)_3}{Si}}\text{-}O]_2\text{-}Si(CH_3)_3}$$

III - 8



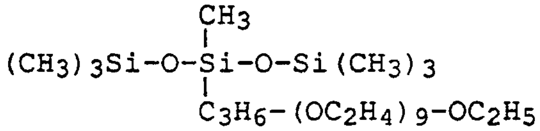
$$\mathrm{(CH_3)_3Si\text{-}O\text{-}[\overset{CH_3}{\underset{C_3H_6\text{-}(OC_2H_4)_9\text{-}Si(CH_3)_3}{Si}}\text{-}O]_3\text{-}Si(CH_3)_3}$$

III - 9



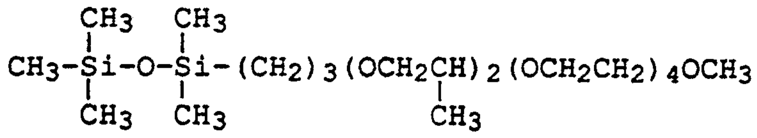
$$\mathrm{(CH_3)_3Si\text{-}O\text{-}[\overset{CH_3}{\underset{C_3H_6\text{-}(OC_2H_4)_{10}\text{-}Si(C_2H_5)_3}{Si}}\text{-}O]_2\text{-}Si(CH_3)_3}$$

III - 10



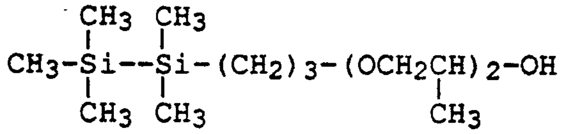
$$\mathrm{(CH_3)_3Si\text{-}O\text{-}\overset{CH_3}{\underset{C_3H_6\text{-}(OC_2H_4)_9\text{-}OC_2H_5}{Si}}\text{-}O\text{-}Si(CH_3)_3}$$

III - 11



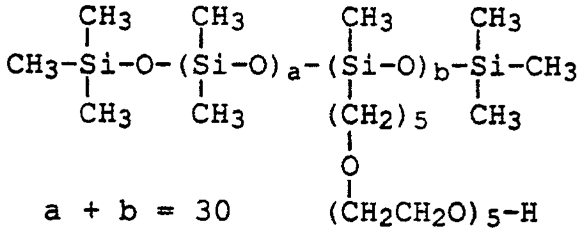
$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3(OCH_2\underset{CH_3}{C}H)_2(OCH_2CH_2)_4OCH_3}$$

III - 12



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{Si}}--\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3-(OCH_2\underset{CH_3}{C}H)_2-OH}$$

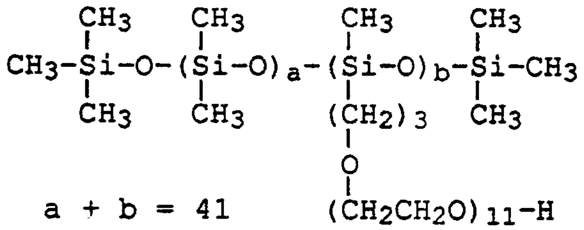
III - 13



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-(\underset{CH_3}{\overset{CH_3}{Si}}-O)_a-(\underset{\begin{array}{c}(CH_2)_5\\ |\\ O\\ |\\ (CH_2CH_2O)_5-H\end{array}}{\overset{CH_3}{Si}}-O)_b-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3}$$

$a + b = 30$

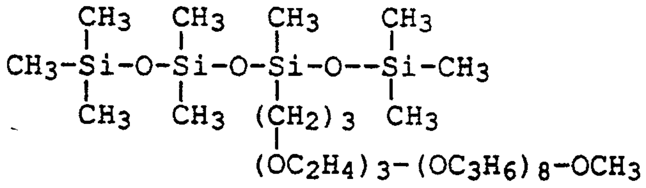
III - 14



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-(\underset{CH_3}{\overset{CH_3}{Si}}-O)_a-(\underset{\begin{array}{c}(CH_2)_3\\ |\\ O\\ |\\ (CH_2CH_2O)_{11}-H\end{array}}{\overset{CH_3}{Si}}-O)_b-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3}$$

$a + b = 41$

III - 15



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{\begin{array}{c}(CH_2)_3\\ |\\ (OC_2H_4)_3-(OC_3H_6)_8-OCH_3\end{array}}{\overset{CH_3}{Si}}-O--\underset{CH_3}{\overset{CH_3}{Si}}-CH_3}$$

When the amount of these water-soluble organic siloxane type compounds to be added is in the range of 0.01 to 20 g per liter of the stabilizing solution, good effect can be exhibited.

If the amount is less than 0.01 g, stain on a light-sensitive material surface becomes conspicuous, and if the amount is more than 20 g, a large amount of the organic siloxane type compound is attached to a light-sensitive material surface, whereby the surface is stained.

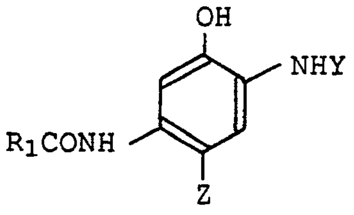
The water-soluble organic siloxane type compounds of the present invention are common water-soluble organic siloxane type compounds as disclosed in Japanese Unexamined Patent Publication No. 18333/1972, Japanese Patent Publication No. 51172/1980, Japanese Patent Publication No. 37538/1976, Japanese Unexamined Patent Publication No. 62128/1974 and U.S. Patent No. 3,545,970.

These water-soluble organic siloxane type compounds are commercially available from Union Carbide Co. and Shin-etsu Kagaku Kogyo K.K.

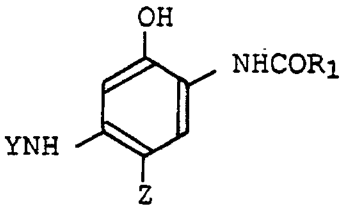
The light-sensitive material according to the present invention may be either of a coupler-in-emulsion type development system in which a coupler is contained in a light-sensitive material (see U.S. Patents No. 2,376,679 and No. 2,801,171) or of a coupler-in-developer type development system in which a coupler is contained in a developing solution (see U.S. Patents No. 2,252,718, No. 2,592,243 and No. 2,590,970). As a coupler, any coupler generally known in the art can be used. For example, as a cyan coupler, cyan couplers outside the scope of the present invention may be used in combination, and said cyan couplers used in combination may include those which are based on a naphthol or phenol structure and form an indoaniline dye by coupling. As a magenta coupler, there may be used magenta couplers having a 5-pyrazolone ring having an active methylene group as a skeletal structure and pyrazoloazole type magenta couplers. As a yellow coupler, there may be used yellow couplers having an active methylene group and having a benzoylacetanilide, pivalylacetanilide or acylacetanilide structure, which may have a substituent group or no substituent group at a coupling position.

Thus, either so-called diequivalent couplers or so-called tetraequivalent couplers can be used as a coupler.

When the light-sensitive color photographic material is a light-sensitive material for negative images (e.g. a color negative film), the preferred cyan coupler may include those represented by the following formulae (C-A), (C-B) and (C-C).

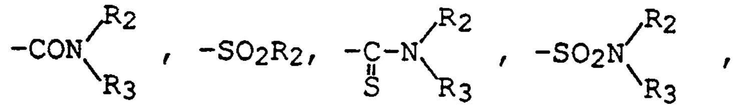


(C-A)



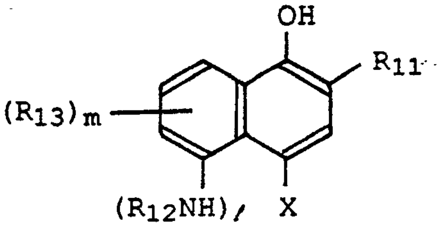
(C-B)

wherein R_1 represents an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or a heterocyclic group; Y represents a group represented by



$$-\mathrm{CON}\begin{matrix}R_2\\R_3\end{matrix},\quad -\mathrm{SO_2R_2},\quad -\underset{\underset{\displaystyle S}{\|}}{C}-\mathrm{N}\begin{matrix}R_2\\R_3\end{matrix},\quad -\mathrm{SO_2N}\begin{matrix}R_2\\R_3\end{matrix},$$

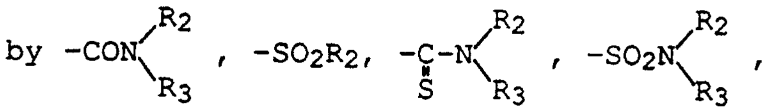
-CONHCOR$_2$ or -CONHSO$_2$R$_2$ (where R_2 represents an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or a heterocyclic group; R_3 represents a hydrogen atom or a group represented by R_2; and R_2 and R_3 may be the same or different and may be bonded to each other to form a 5- or 6-membered hetero ring); and Z represents a hydrogen atom or a group which can be eliminated by coupling reaction with an oxidized product of an aromatic primary amine type color developing agent.



(C-C)

wherein R_{11} represents $-CONR_{14}R_{15}$, $-NHCOR_{14}$, $-NHCOOR_{16}$, $-NHSO_2R_{16}$, $-NHCONR_{14}R_{15}$ or $-NHSO_2NR_{14}R_{15}$; R_{12} represents a monovalent group; R_{13} represents a substituent group; X represents a hydrogen atom or a group which can be eliminated by coupling reaction with an oxidized product of an aromatic primary amine type color developing agent; ℓ represents 0 or 1; m represents 0 to 3; R_{14} and R_{15} each represent a hydrogen atom, an aromatic group, an aliphatic group or a heterocyclic group; R_{16} represents an aromatic group, an aliphatic group or a heterocyclic group; when m is 2 or 3, the respective R_{13}'s may be the same or different and may be bonded to each other to form a ring; R_{14} and R_{15}, R_{12} and R_{13}, and R_{12} and X may be bonded to each other to form a ring, respectively; and when ℓ is 0, m is 0 and R_{11} is - $CONHR_{17}$ where R_{17} represents an aromatic group.

First, the formula (C-A) and the formula (C-B) shown above are explained. In said formulae, Y is a group represented



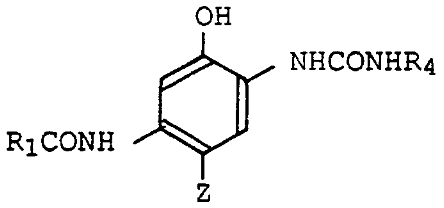
$$\text{by } -CON\begin{matrix}R_2\\R_3\end{matrix},\ -SO_2R_2,\ -\underset{\underset{S}{\|}}{C}-N\begin{matrix}R_2\\R_3\end{matrix},\ -SO_2N\begin{matrix}R_2\\R_3\end{matrix},$$

$-CONHCOR_2$ or $-CONHSO_2R_2$. Here, R_1 and R_2 each represent an alkyl group, preferably an alkyl group having 1 to 20 carbon atoms (e.g. each group of methyl, ethyl, t-butyl and dodecyl), an alkenyl group, preferably an alkenyl group having 2 to 20 carbon atoms (an allyl group and a heptadecenyl group), a cycloalkyl group, preferably 5- to 7-membered cyclic groups (e.g. cyclohexyl), an aryl group (e.g. a phenyl group, a tolyl group and a naphthyl group) and a heterocyclic group, preferably a 5- or 6-membered cyclic group containing 1 to 4 nitrogen atoms, oxygen atoms or sulfur atoms (e.g. a furyl group, a thienyl group and a benzothiazolyl group). R_3 represents a hydrogen atom or a group represented by R_2. R_2 and R_3 may be bonded to each other to form a 5- or 6-membered hetero ring. Into R_1 and R_2, any desired substituent group can be introduced, and may include, for example, an alkyl group having 1 to 10 carbon atoms (e.g. methyl, i-propyl, i-butyl, t-butyl and t-octyl), an aryl group (e.g. phenyl and naphthyl), a halogen atom (fluorine, chlorine and bromine), a cyano group, a nitro group, a sulfonamide group (e.g. methanesulfonamide, butanesulfonamide and p-toluenesulfonamide), a sulfamoyl group (methylsulfamoyl and phenylsulfamoyl), a sufonyl group (e.g. methanesulfonyl and p-toluenesulfonyl), a fluorosulfonyl group, a carbamoyl group (e.g. dimethylcarbamoyl and phenylcarbamoyl), an oxycarbonyl group (e.g. ethoxycarbonyl and phenoxycabonyl) an acyl group (e.g. acetyl and benzoyl), a hetero ring (e.g. a pyridyl group and a pyrazolyl group), an alkoxy group, an aryloxy group and an acyloxy group.

In the formula (C-A) and the formula (C-B), R_1 represents a ballast group necessary for imparting diffusion-proof property to the cyan couplers represented by the formula (C-A) and the formula (C-B) and cyan dyes formed from said cyan couplers. R_1 may be preferably an alkyl group having 4 to 30 carbon atoms, an aryl group, an alkenyl group, a cycloalkyl group or a heterocyclic group, and, for example, a straight or branched alkyl group (e.g. t-butyl, n-octyl, t-octyl and n-dodecyl) and a 5- or 6-membered heterocyclic group.

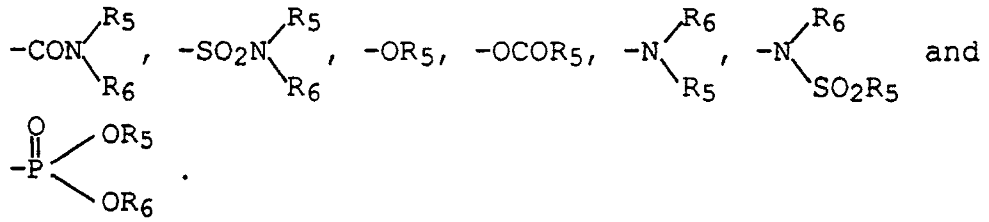
In the formula (C-A) and the formula (C-B), Z represents a hydrogen atom or a group which can be eliminated by coupling reaction with an oxidized product of a color developing agent. Z may include, for example, a halogen atom (e.g. chlorine, bromine and fluorine), a substituted or unsubstituted alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, a sulfonyloxy group, an alkylthio group, an arylthio group, a heterocyclic thio group and a sulfonamide group, and further, as a specific example thereof, there may be mentioned those disclosed in U.S. Patent No. 3,741,563, Japanese Unexamined Patent Publication No. 37425/1972, Japanese Patent Publication No. 36894/1973, Japanese Unexamined Patent Publications No. 10135/1975, No. 117422/1975, No. 130441/1975, No. 108841/1976, No. 120343/1975, No. 18315/1977, No. 105226/1978, No. 14736/1979, No. 48237/1979, No. 32071/1980, No. 65957/1980, No. 1938/1981, No. 12643/1981, No. 27147/1981, No. 146050/1984, No. 166956/1984, No. 24547/1985, No. 35731/1985 and No. 37557/1985.

In the present invention, the cyan coupler represented by the formula (C-D) is preferred.



(C-D)

In the formula (C-D), R_4 is a substituted or unsubstituted aryl group (particularly preferably a phenyl group). When said aryl group has a substituent group, the substituent group may include at least one substituted group selected from SO_2R_5, a halogen atom (fluorine, chlorine and bromine), $-CF_3$, $-NO_2$, -CN, $-COR_5$, $-COOR_5$, $-SO_2OR_5$,

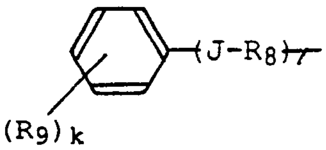


$$-CON\begin{matrix}R_5\\R_6\end{matrix},\ -SO_2N\begin{matrix}R_5\\R_6\end{matrix},\ -OR_5,\ -OCOR_5,\ -N\begin{matrix}R_6\\R_5\end{matrix},\ -N\begin{matrix}R_6\\SO_2R_5\end{matrix}\ \text{and}\ -\overset{O}{\overset{\|}{P}}\begin{matrix}OR_5\\OR_6\end{matrix}.$$

Here, R_5 represents an alkyl group, preferably an alkyl group having 1 to 20 carbon atoms (e.g. each group of methyl, ethyl, t-butyl and dodecyl), an alkenyl group, preferably an alkenyl group having 2 to 20 carbon atoms (an allyl group and a heptadecenyl group), a cycloalkyl group, preferably 5- to 7-membered cyclic groups (e.g. cyclohexyl) and an aryl group (e.g. a phenyl group, a tolyl group and a naphthyl group), and R_6 is a hydrogen atom or a group represented by R_5.

A suitable compound of the cyan coupler of the present invention represented by the formula (C-D) is a compound in which R_4 is a substituted or unsubstituted phenyl group, and a substituent group of the phenyl group is cyano group, nitro group, $-SO_2R_7$ (where R_7 is an alkyl group), a halogen atom or trifluoromethyl group.

In the formula (C-D), Z and R_1 each have the same meanings of those in the formulae (C-A) and (C-B). A preferred example of the ballast group represented by R_1 is a group represented by the following formula (C-E).



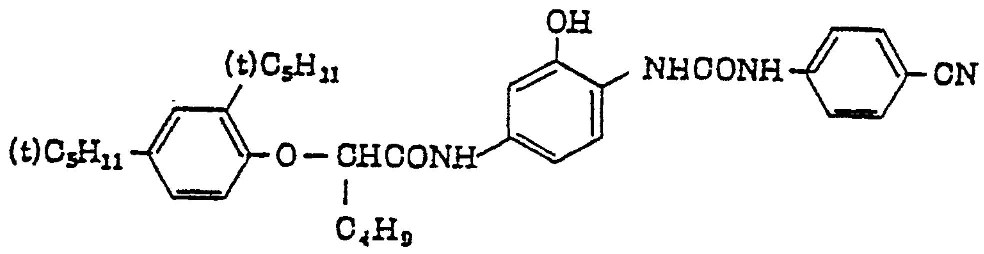
(C-E)

wherein J represents an oxygen atom, a sulfur atom or a sulfonyl group; K represents an integer of 0 to 4; ℓ represents 0 or 1; when K is 2 or more, two or more R_9's may be the same or different; R_8 represents a straight or branched substituted alkylene group having 1 to 20 carbon atoms such as an aryl group; R_9 represents a monovalent group, preferably a hydrogen atom, a halogen atom (e.g. chlorine and bromine), an alkyl group, preferably a straight or branched alkyl group having 1 to 20 carbon atoms (e.g. each group of methyl, t-butyl, t-pentyl, t-octyl, dodecyl, pentadecyl, benzyl and phenethyl), an aryl group (e.g. a phenyl group), a heterocyclic group (e.g. a nitrogen-containing heterocyclic group), an alkoxy group, preferably a straight or branched alkoxy group having 1 to 20 carbon atoms (e.g. each group of methoxy, ethoxy, t-butyloxy, octyloxy, decyloxy and dodecyloxy), an aryloxy group (e.g. a phenoxy group), a hydroxy group, an acyloxy group, preferably an alkylcarbonyloxy group, an arylcarbonyloxy group (e.g. an acetoxy group and a benzoyloxy group), a carboxy group, an alkyloxycarbonyl group, preferably a straight or branched alkylcarbonyl group having 1 to 20 carbon atoms, preferably a phenoxycarbonyl group, an alkylthio group, preferably an acyl group having 1 to 20 carbon atoms, preferably a straight or branched alkylcarbonyl group having 1 to 20 carbon atoms, an acylamino group, preferably a straight or branched alkylcarboamide group having 1 to 20 carbon atoms, a benzenecarboamide group, a sulfonamide group, preferably a straight or branched alkylsulfonamide group or benzenesulfonamide group having 1 to 20 carbon atoms, a carbamoyl group, preferably a straight or branched alkylaminocarbonyl group or phenylaminocarbonyl group having 1 to 20 carbon atoms and a sulfamoyl group, preferably a straight or branched alkylaminosulfonyl group or phenylaminosulfonyl group having 1 to 20 carbon atoms.

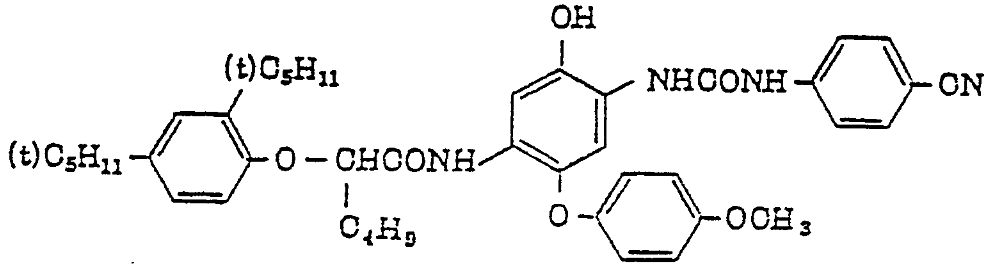
Next, specific exemplary compounds of the cyan coupler of the present invention represented by the formula (C-A) or (C-B) are shown, but the present invention is not limited to these.

(Exemplary compounds)

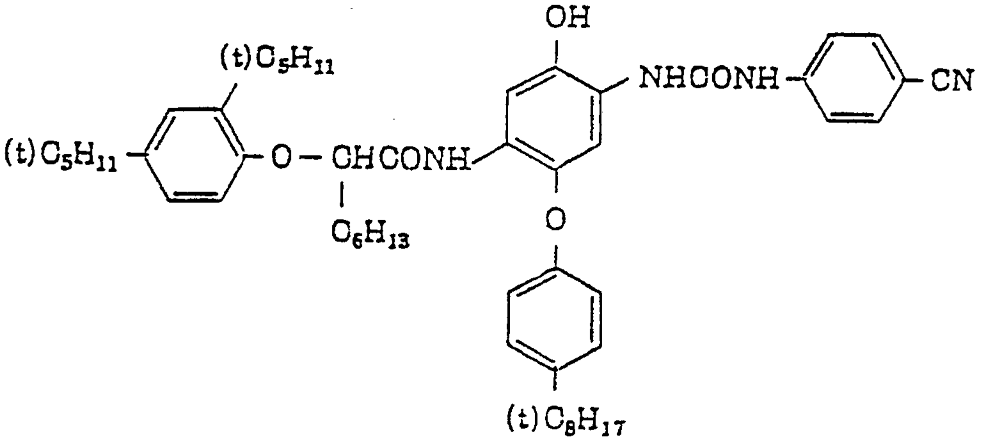
C − 1



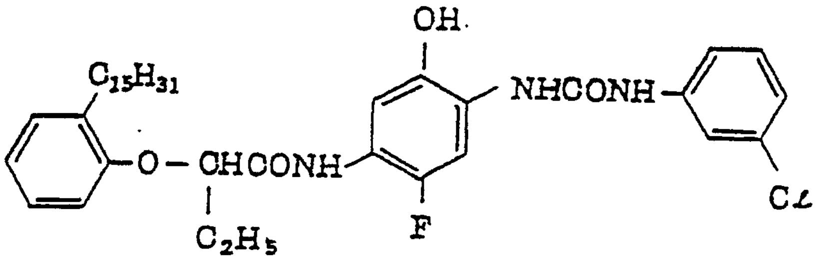
C − 2



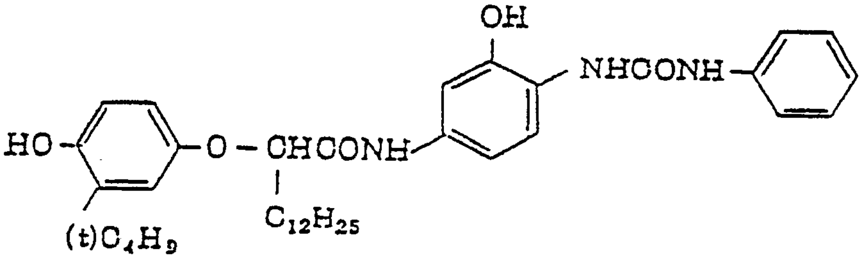
C − 3



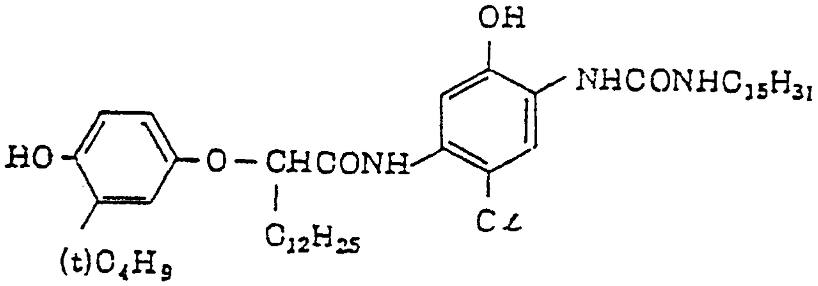
O – 4



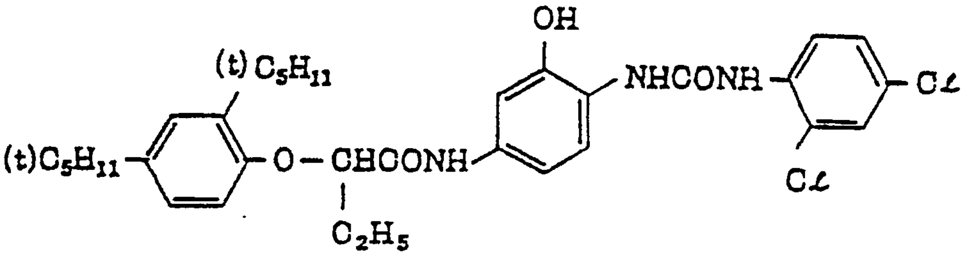
O – 5



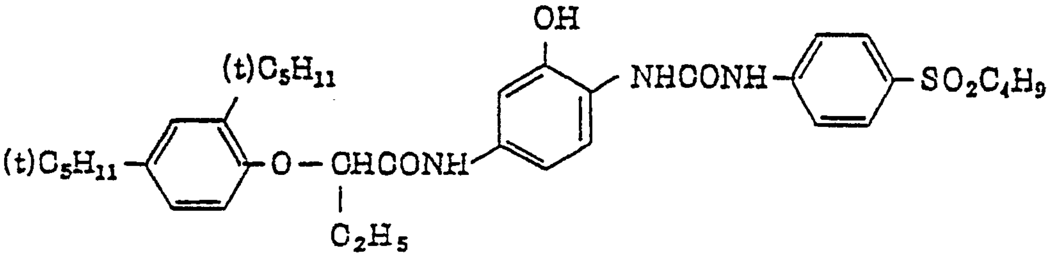
O – 6



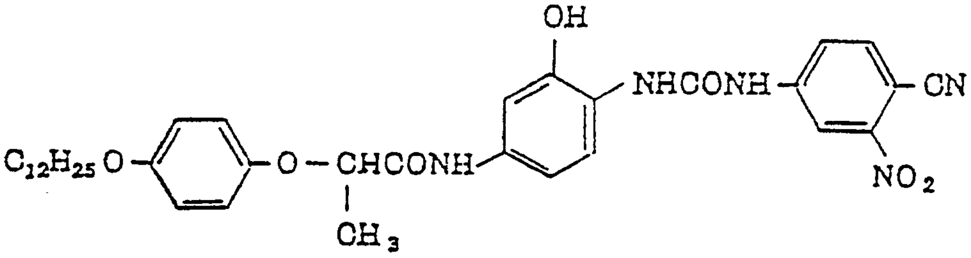
C − 7



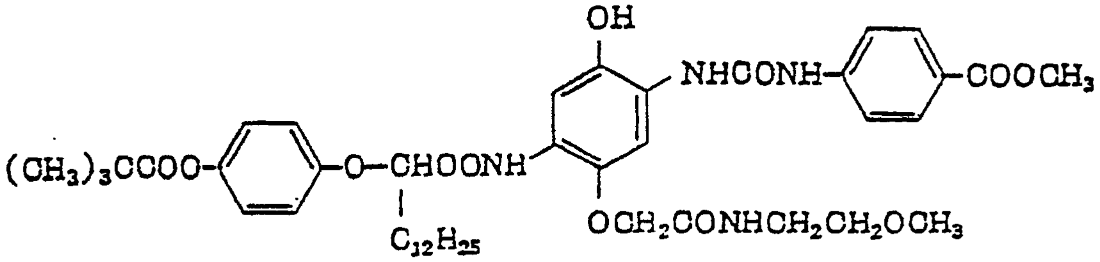
C − 8



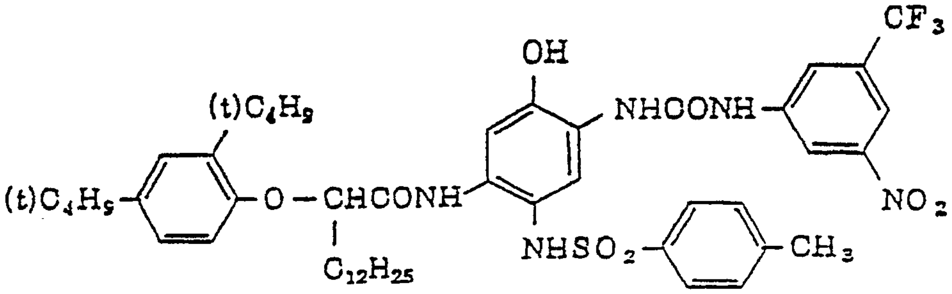
C − 9



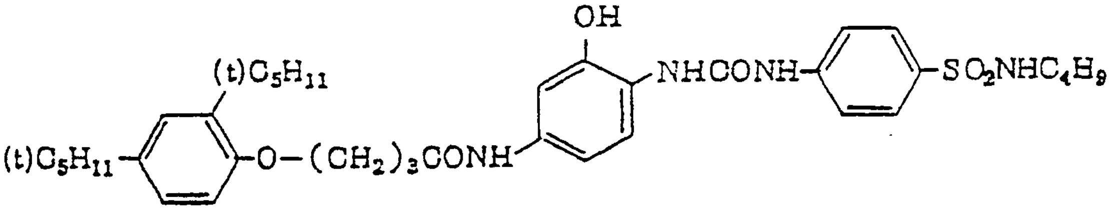
C－13


OH
NHCONH
COOCH3
(CH3)3COOO
O—CHOONH
C12H25
OCH2CONHCH2CH2OCH3

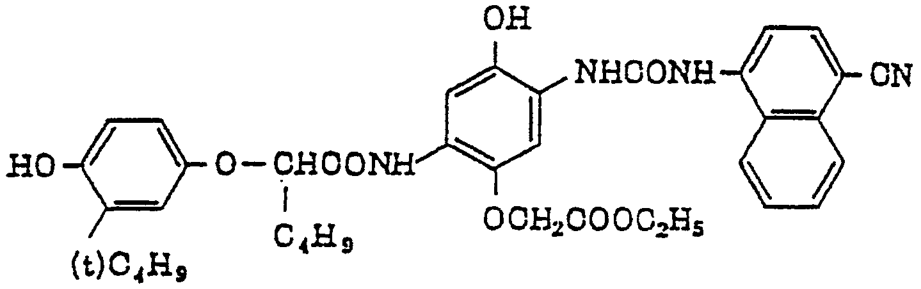
C－14


CF3
OH
NHCONH
(t)C4H9
(t)C4H9
O—CHCONH
NO2
C12H25
NHSO2
CH3

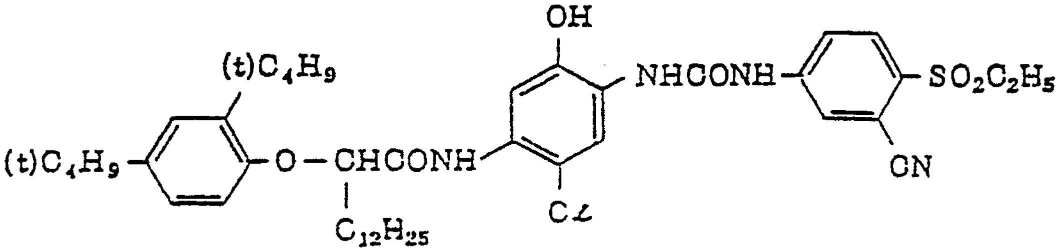
C－15


OH
NHCONH
SO2NHC4H9
(t)C5H11
(t)C5H11
O—(CH2)3CONH

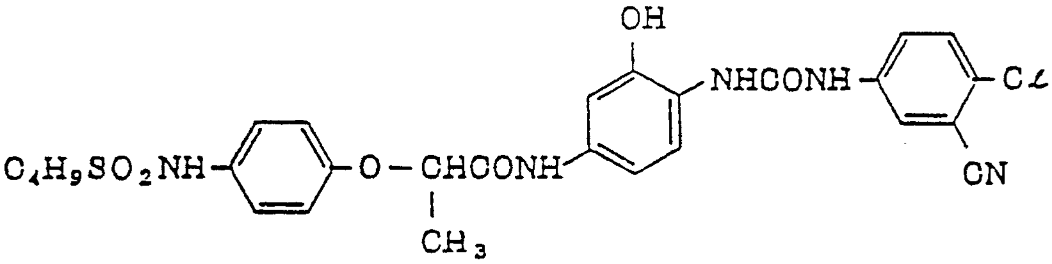
C－10



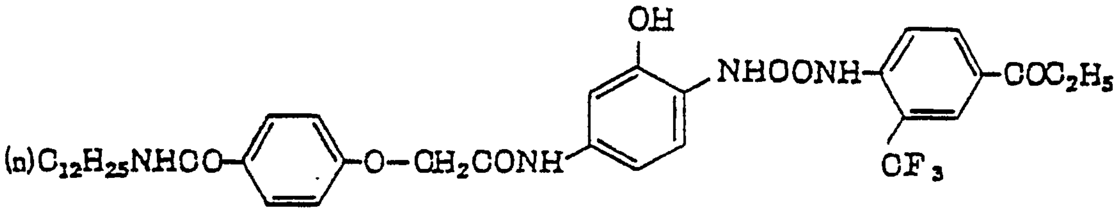
C－11



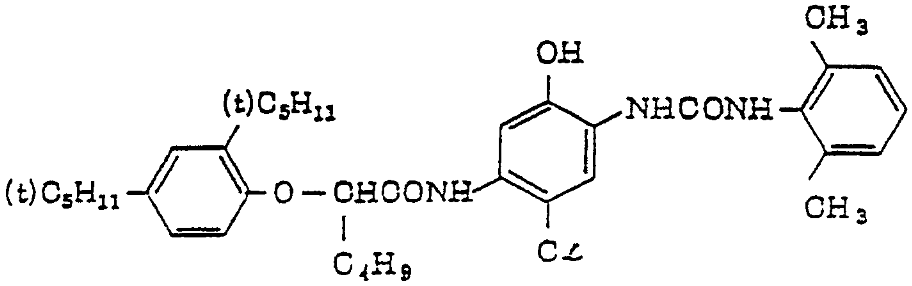
C－12



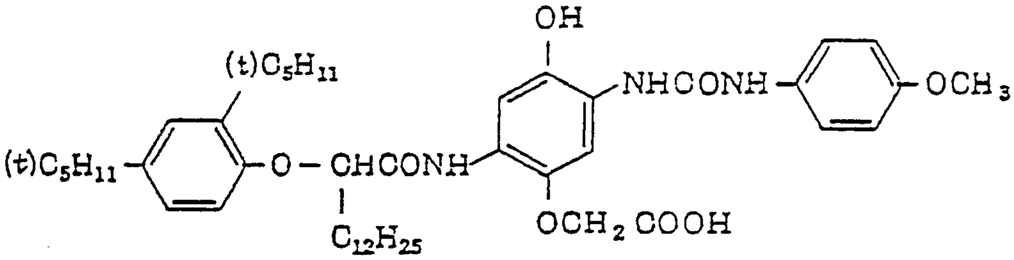
C − 1 6


OH
NHOONH
COC$_2$H$_5$
CF$_3$
(n)C$_{12}$H$_{25}$NHCO
O−CH$_2$CONH

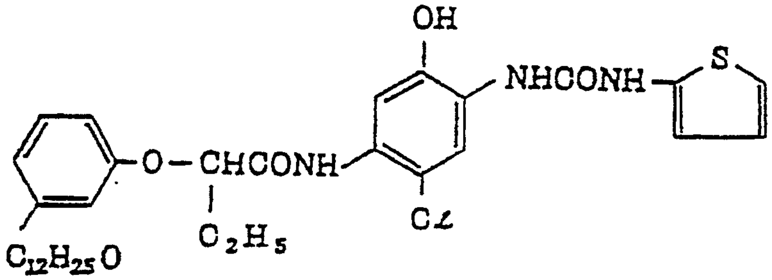
C − 1 7


CH$_3$
OH
(t)C$_5$H$_{11}$
NHCONH
(t)C$_5$H$_{11}$
O − CHCONH
CH$_3$
C$_4$H$_9$
Cℓ

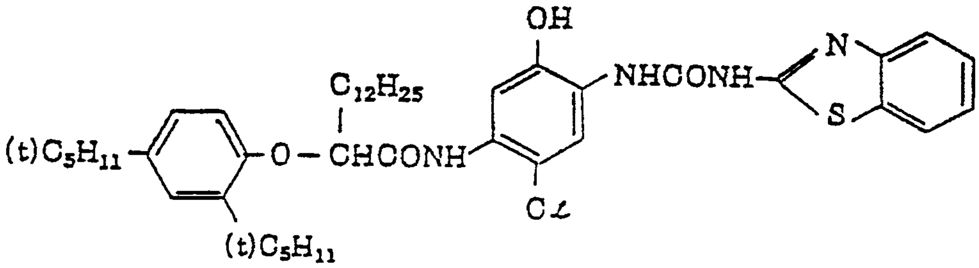
C − 1 8


OH
(t)C$_5$H$_{11}$
NHCONH
OCH$_3$
(t)C$_5$H$_{11}$
O − CHCONH
C$_{12}$H$_{25}$
OCH$_2$COOH

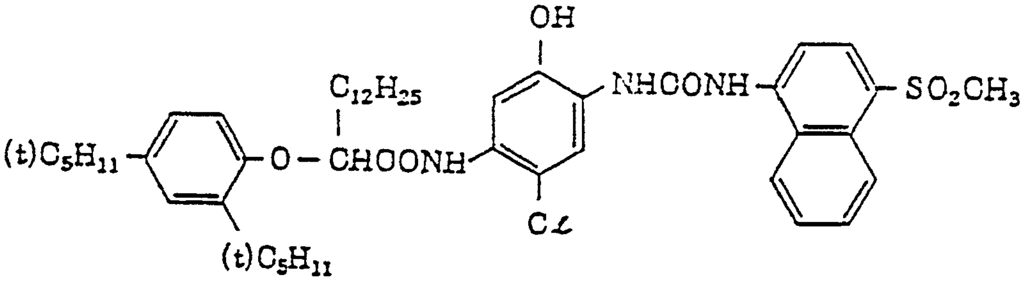
C − 19


OH
NHCONH
S
O
CHCONH
C_2H_5
$C_{12}H_{25}O$
Cl

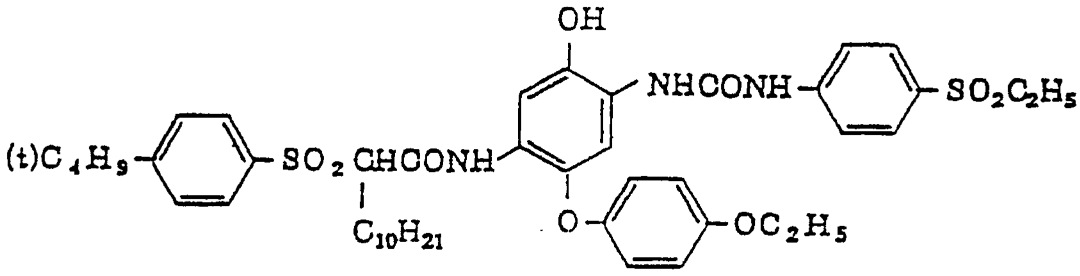
C − 20


OH
NHCONH
N
S
$C_{12}H_{25}$
(t)C_5H_{11}
O
CHCONH
(t)C_5H_{11}
Cl

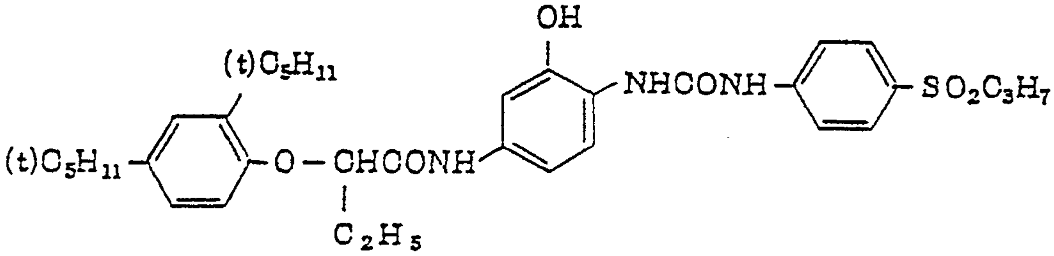
C − 21


OH
NHCONH
SO_2CH_3
$C_{12}H_{25}$
(t)C_5H_{11}
O
CHCONH
(t)C_5H_{11}
Cl

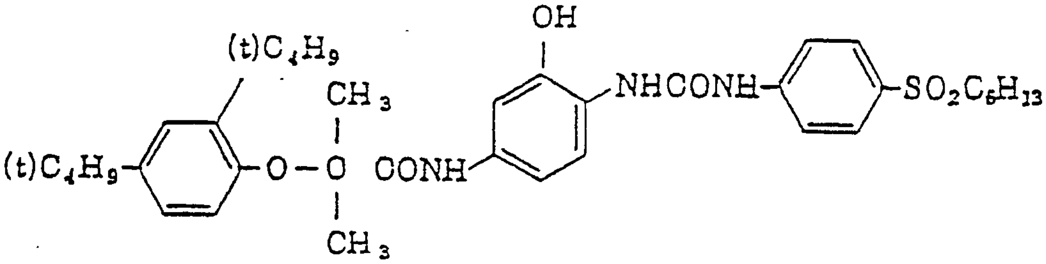
C－２２



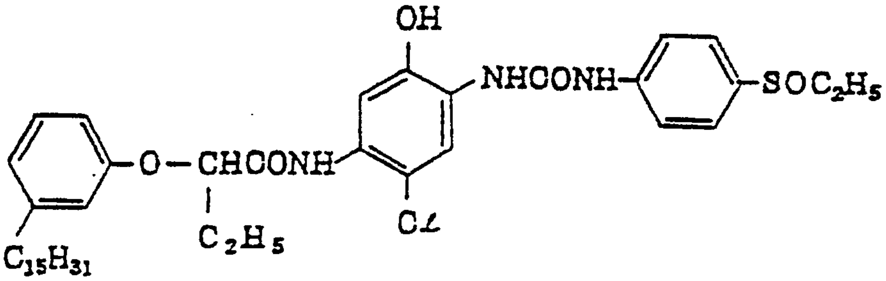
C－２３



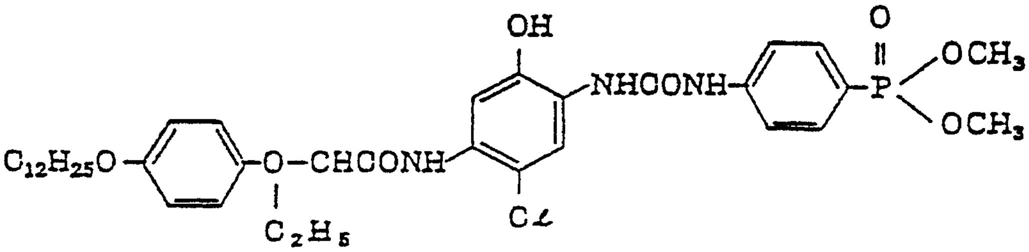
C－２４



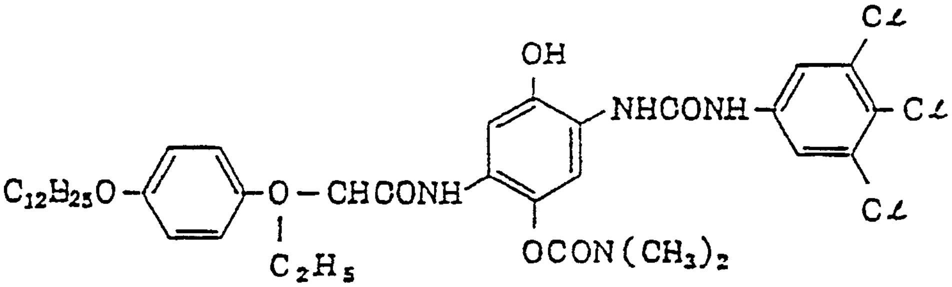
O－25


OH
NHCONH
SOC₂H₅
O－CHCONH
C₂H₅
Cℓ
C₁₅H₃₁

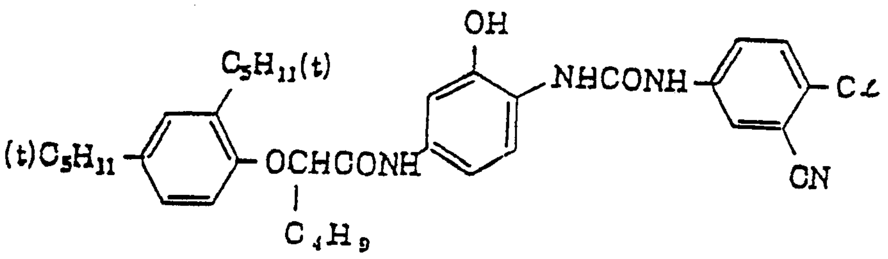
O－26


OH
NHCONH
O
P
OCH₃
OCH₃
C₁₂H₂₅O
O－CHCONH
C₂H₅
Cℓ

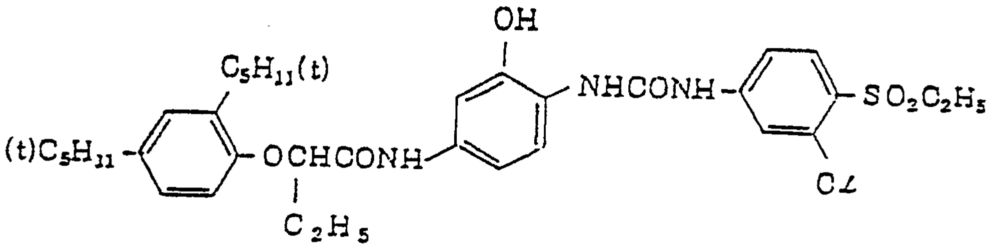
O－27


Cℓ
OH
NHCONH
Cℓ
Cℓ
C₁₂H₂₅O
O－CHCONH
C₂H₅
OCON(CH₃)₂

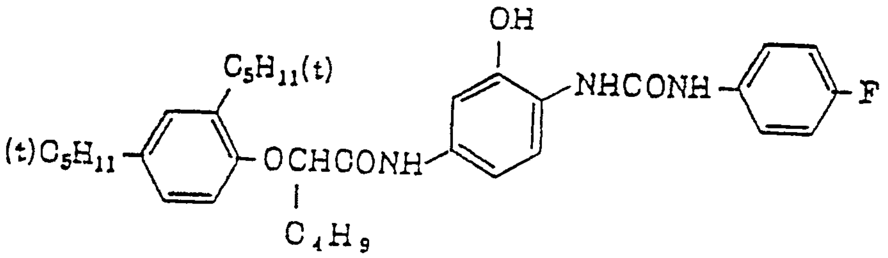
C-28



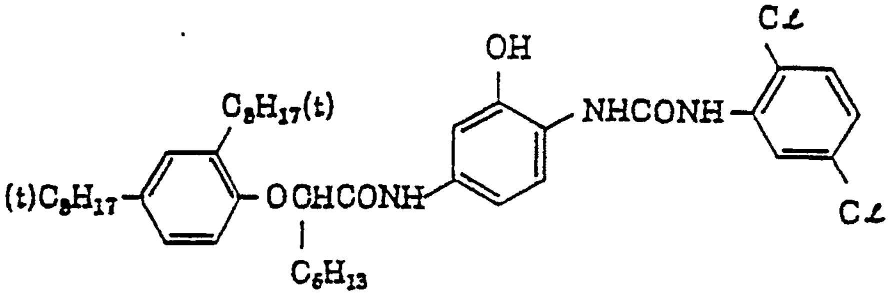
C-29



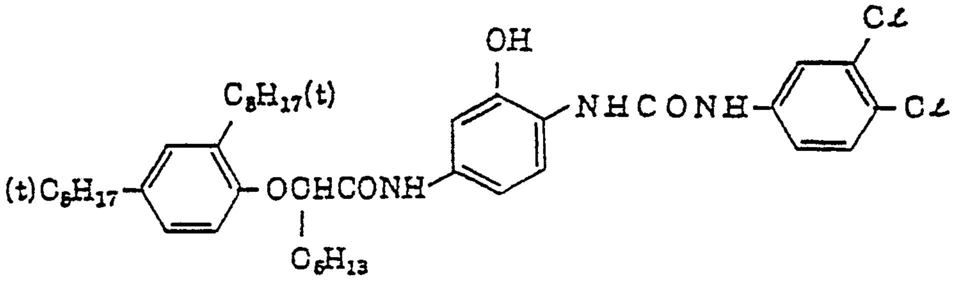
C-30



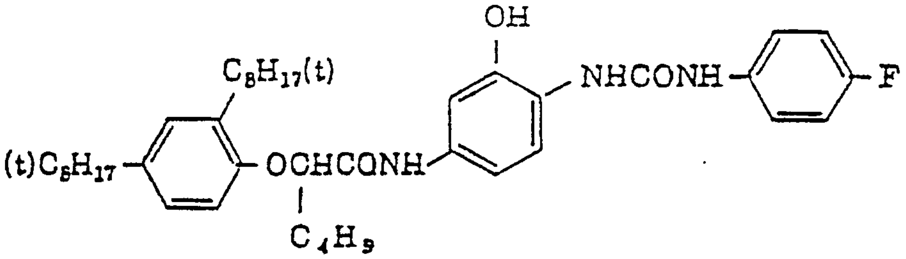
C－31


OH
Cℓ
$C_8H_{17}(t)$
NHCONH
$(t)C_8H_{17}$
OCHCONH
C_6H_{13}
Cℓ

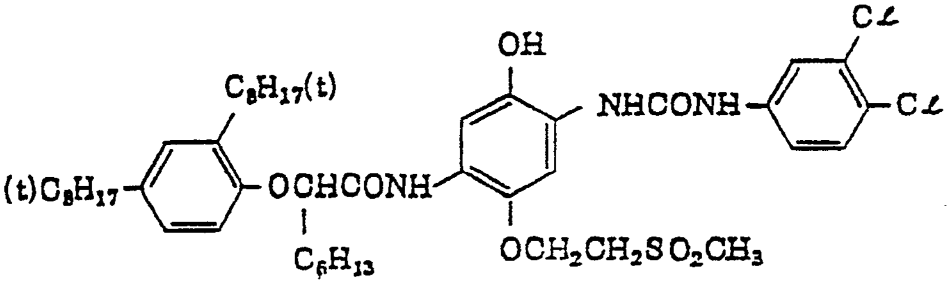
C－32


Cℓ
OH
$C_8H_{17}(t)$
NHCONH
Cℓ
$(t)C_8H_{17}$
OCHCONH
C_6H_{13}

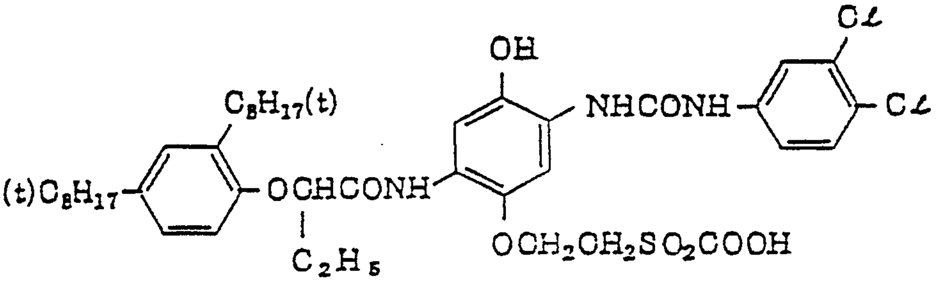
C－33


OH
$C_8H_{17}(t)$
NHCONH
F
$(t)C_8H_{17}$
OCHCONH
C_4H_9

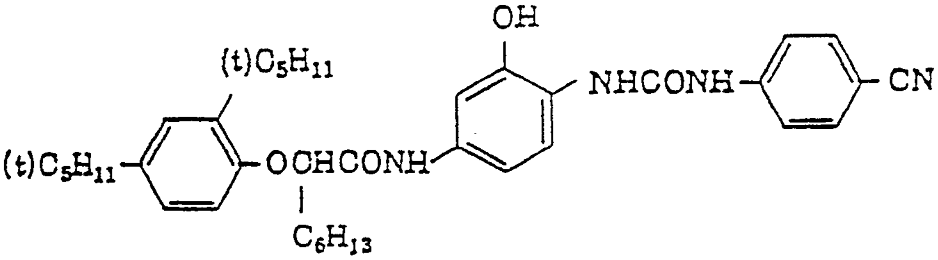
O－34


OH
Cℓ
Cℓ
$C_8H_{17}(t)$
NHCONH
$(t)C_8H_{17}$
OCHCONH
C_6H_{13}
$OCH_2CH_2SO_2CH_3$

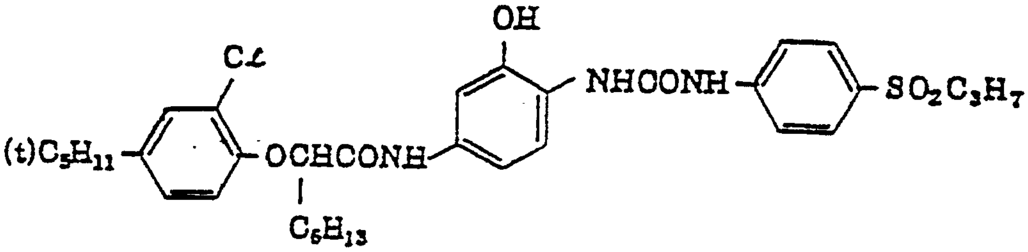
O－35


OH
Cℓ
Cℓ
$C_8H_{17}(t)$
NHCONH
$(t)C_8H_{17}$
OCHCONH
C_2H_5
$OCH_2CH_2SO_2COOH$

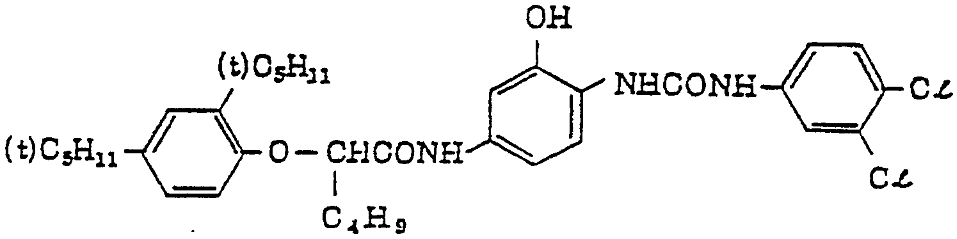
O－36


OH
$(t)C_5H_{11}$
NHCONH
CN
$(t)C_5H_{11}$
OCHCONH
C_6H_{13}

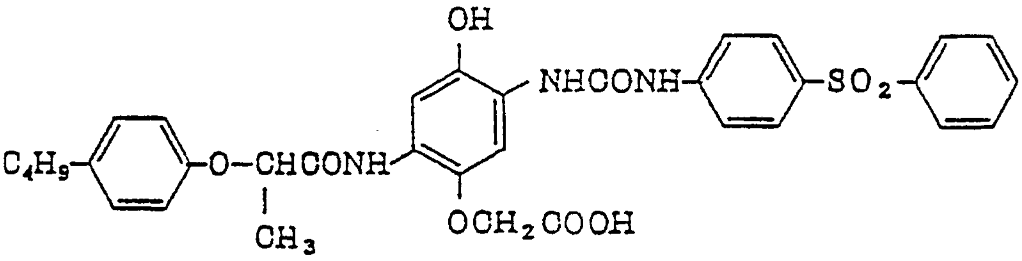
C-37


OH
Cℓ
NHCONH
SO2C3H7
(t)C5H11
OCHCONH
C6H13

C-38


OH
(t)C5H11
NHCONH
Cℓ
(t)C5H11
O−CHCONH
C4H9
Cℓ

C-39


OH
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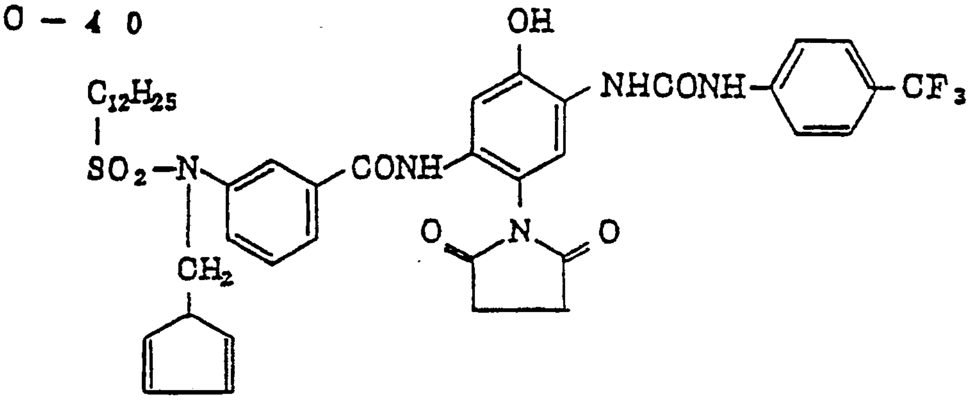
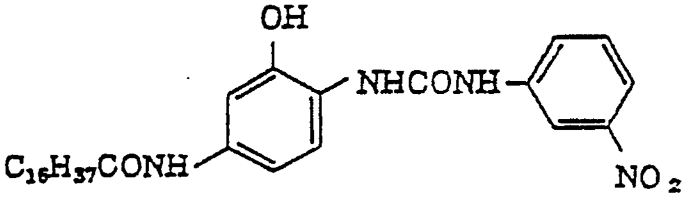
C4H9
O−CHCONH
CH3
OCH2COOH

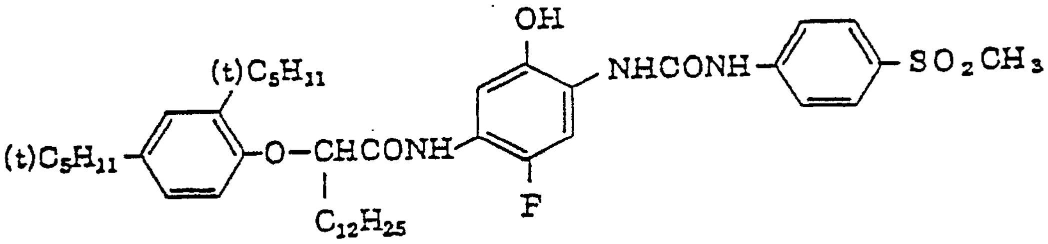
O－40



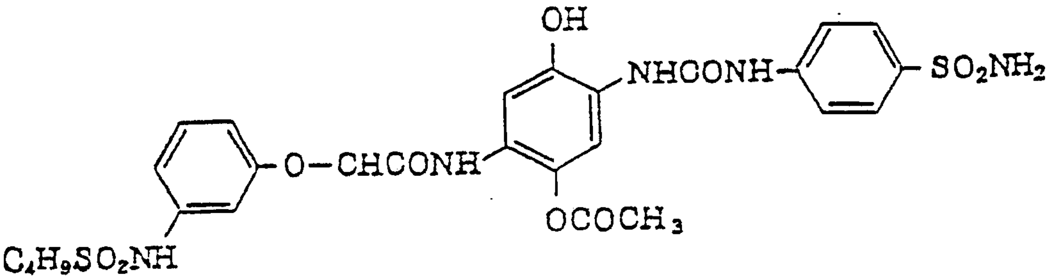
O－41



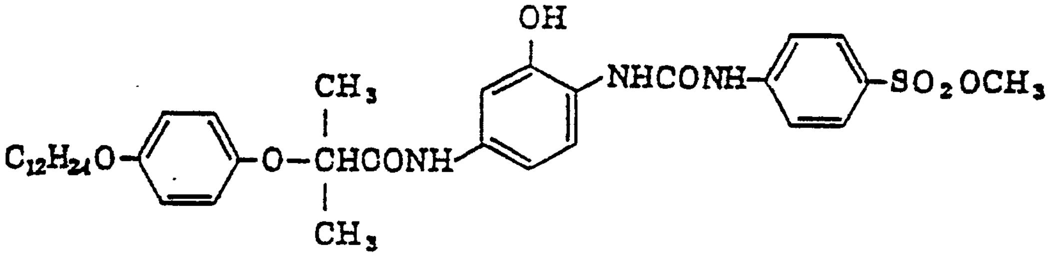
O－42



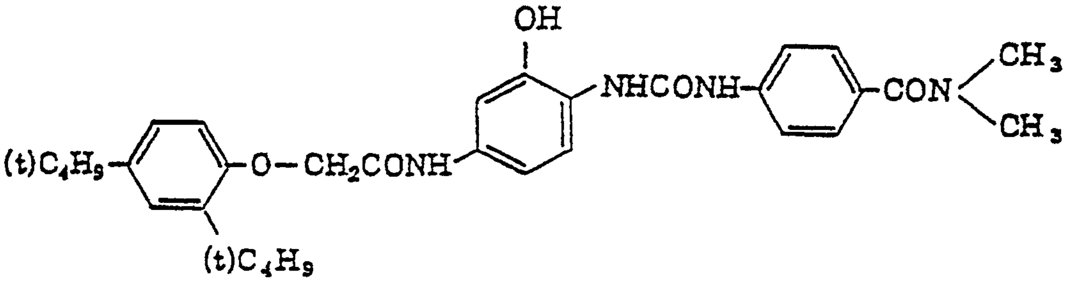
O－43



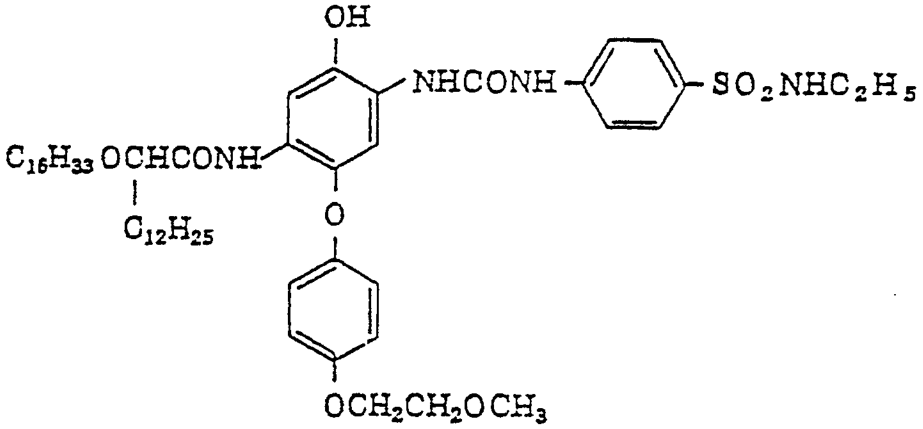
C－44



C－45



C－46

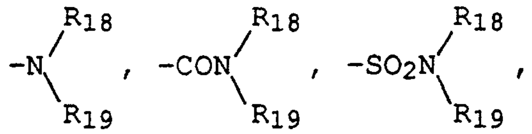


Next, the above formula (CC) is described.

Each group represented by R_{12} to R_{17} in the formula (C-C) may include those having a substituent group.

As R_{16}, an aliphatic group having 1 to 30 carbon atoms, an aromatic group having 6 to 30 carbon atoms and a heterocyclic group having 1 to 30 carbon atoms are preferred, and as R_{14} and R_{15}, a hydrogen atom and those mentioned as a preferred example of R_{16} are preferred.

As R_{12}, preferred are a hydrogen atom which bonded directly or through NH, CO or SO_2 to NH, an aliphatic group having 1 to 30 carbon atoms, an aromatic group having 6 to 30 carbon atoms, a heterocyclic group having 1 to 30 carbon atoms, $-OR_{18}$, $-COR_{18}$,



$$-N{<}^{R_{18}}_{R_{19}}\ ,\quad -CON{<}^{R_{18}}_{R_{19}}\ ,\quad -SO_2N{<}^{R_{18}}_{R_{19}}\ ,$$

$-PO(OR_{20})_2$, $-PO(R_{20})_2$, $-CO_2R_{20}$, $-SO_2R_{20}$ or $-SO_2OR_{20}$ (where R_{18}, R_{19} and R_{20} each have the same meanings of R_{14}, R_{15} and R_{16} defined above; R_{18} and R_{19} may be bonded to form a ring).

R_{17} is preferably an aromatic group having 6 to 30 carbon atoms, and as a representative example of a substituent group of R_{17}, there may be mentioned a halogen atom, a hydroxy group, an amino group, a carboxyl group, a sulfonic acid group, a cyano group, an aromatic group, a heterocyclic group, a carbonamide group, a sulfonamide group, a carbamoyl group, a sulfamoyl group, an ureido group, an acyl group, an acyloxy group, an aliphatic oxy group, an aromatic oxy group, an aliphatic thio group, an aromatic thio group, an aliphatic sulfonyl group, an aromatic sulfonyl group, a sulfamoylamino group, a nitro group, an imide group, an aliphatic group and an aliphatic oxycarbonyl group. When R_{17} is substituted with plural substituent groups, the plural substituent groups may be bonded to each other to form a ring, and as an example thereof, there may be mentioned a dioxymethylene group.

As a representative example of R_{13}, there may be mentioned a halogen atom, a hydroxy group, an amino group, a carboxyl group, a sulfonic acid group, a cyano group, an aromatic group, a heterocyclic group, a carbonamide group, a sulfonamide group, a carbamoyl group, a sulfamoyl group, an ureido group, an acyl group, an acyloxy group, an aliphatic oxy group, an aromatic oxy group, an aliphatic thio group, an aromatic thio group, an aliphatic sulfonyl group, an aromatic sulfonyl group, a sulfamoylamino group, a nitro group and an imide group, and a number of carbon atoms contained in this R_{13} is preferably 0 to 13. When $m = 2$, an example of a cyclic R_{13} is a dioxymethylene group.

When ℓ is 1, R_{11} is particularly preferably $-CONR_{14}R_{15}$, m is preferably 0, and R_{12} is preferably $-COR_{18}$, $-COOR_{20}$, $-SO_2R_{20}$, $-CONR_{18}R_{19}$ and $-SO_2NR_{18}R_{19}$ which are bonded directly to NH, more preferably $-COOR_{20}$, $-COR_{18}$ and $-SO_2R_{20}$ which are bonded directly to NH, and among them most preferably $-COOR_{20}$.

Those which form a polymer such as a dimer or more through R_{11} to R_{13} and X are included in the present invention.

In the formula (C-C), the case where $\ell = 0$ is preferred.

Specific examples of the coupler represented by the formula (C-C) are disclosed in Japanese Unexamined Patent Publications No. 237448/1985, No. 153640/1986, No. 145557/1986, No. 85242/1987, No. 15529/1973, No. 117422/1975, No. 18315/1977, No. 90932/1977, No. 52423/1978, No. 48237/1979, No. 66129/1979, No. 32071/1980, No. 65957/1980, No. 105226/1980, No. 1938/1981, No. 12643/1981, No. 27147/1981, No. 126832/1981 and No. 95346/1983, and U.S. Patent No. 3,488,193, and can be synthesized according to the methods disclosed in these publications.

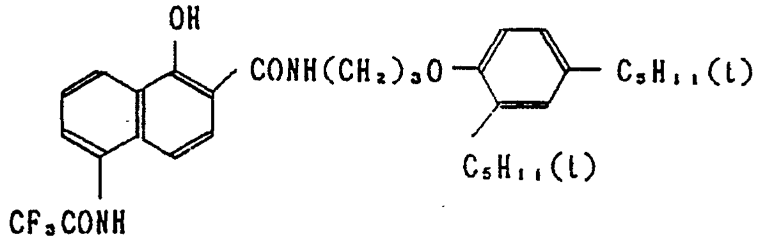
For adding the coupler to a light-sensitive material, depending on physical properties (e.g. solubility) of the coupler, various methods such as the oil-in-water type emulsifying dispersion method in which a water-insoluble high boiling point organic solvent is used, the alkali dispersion method in which a coupler is added.in the form of an alkaline solution, the latex dispersion method and the solid dispersion method in which a coupler is added directly in the form of minute solid can be employed.

The amount of the coupler to be added is generally 1.0×10^{-3} mole to 1.0 mole, preferably in the range of 5.0×10^{-3} mole to 8.0×10^{-1} mole per mole of silver halide.

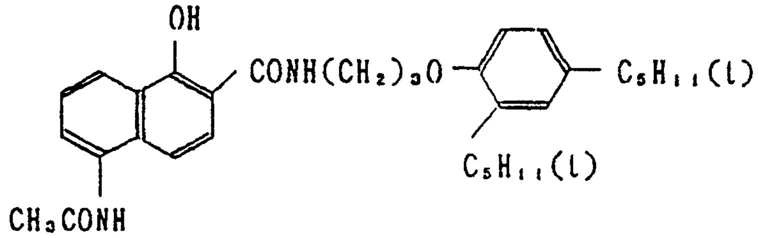
In the following, representative specific examples of the coupler represented by the formula (C-C) are shown, but the present invention is not limited to these.

(Exemplary compounds)

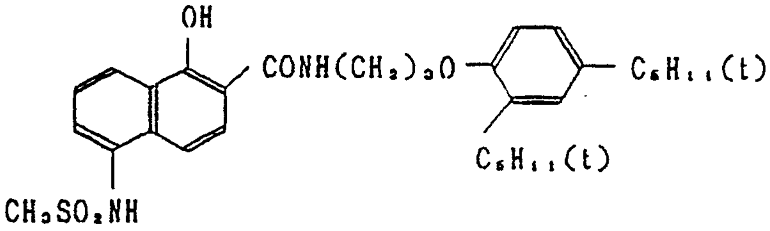
C－5 1



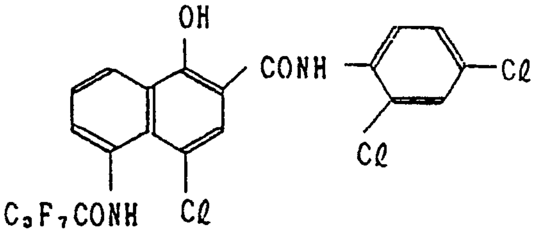
C－5 2



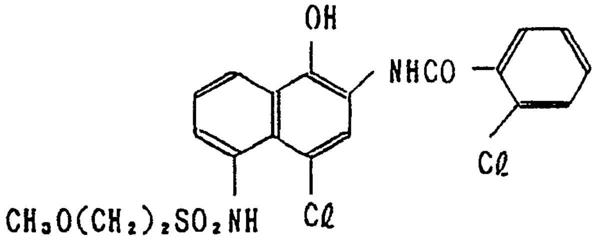
C－5 3



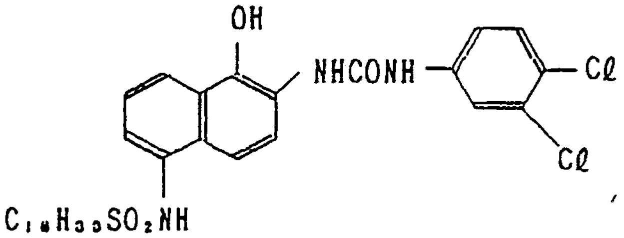
C－5 4



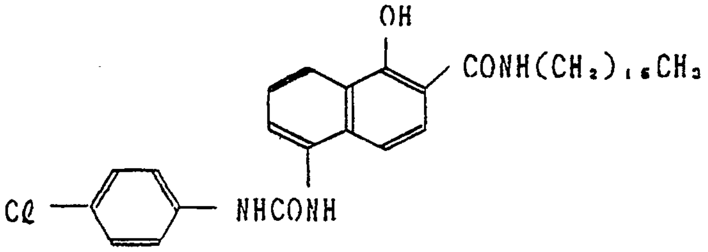
C－55



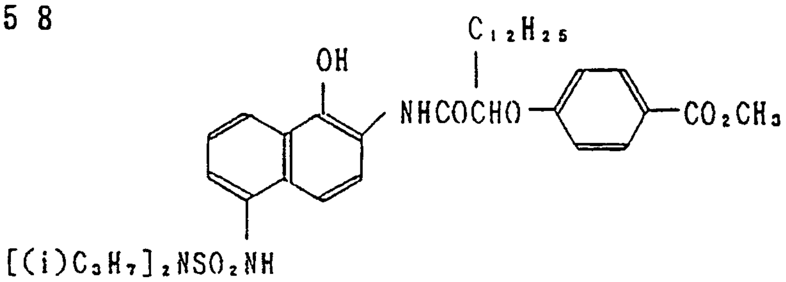
C－56



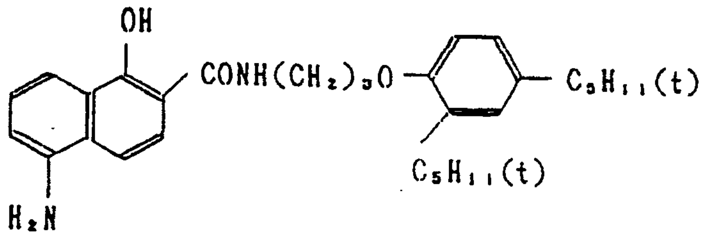
C－57



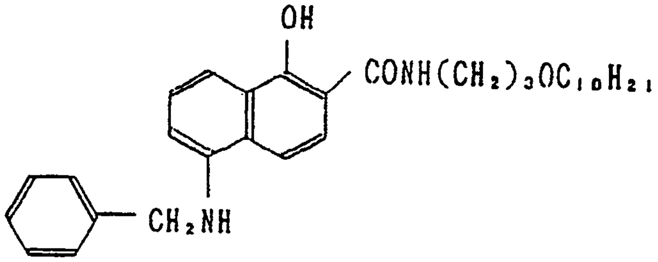
C－58



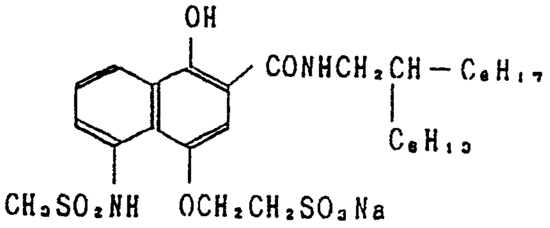
C－５９



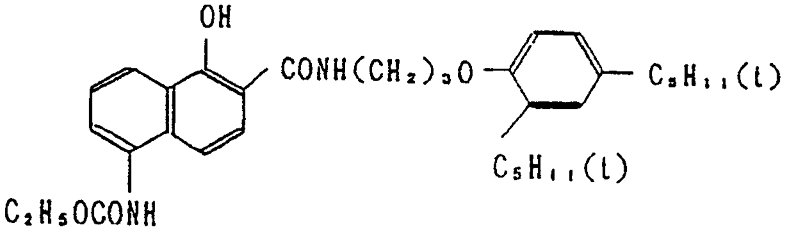
C－６０



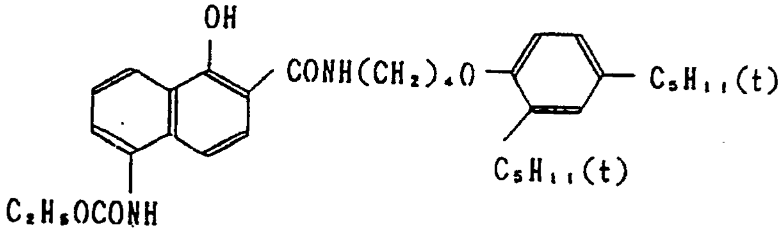
C－６１



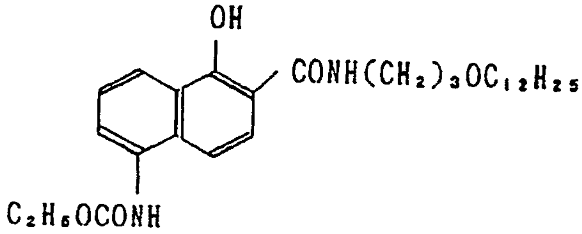
C－６２



C－６３



C－６４



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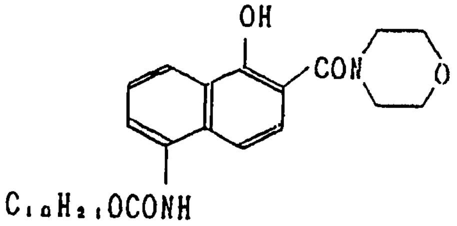

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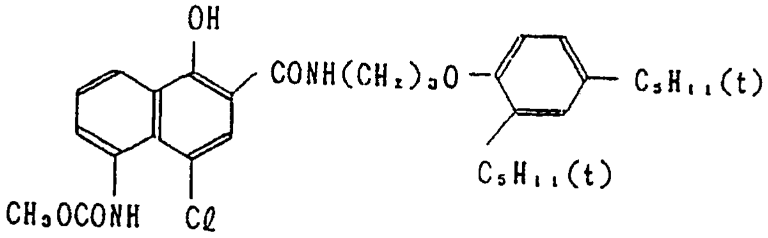
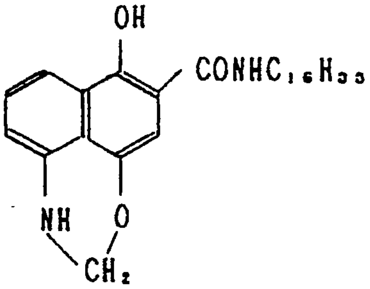
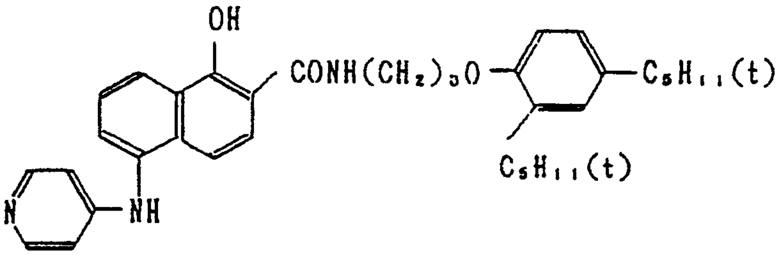


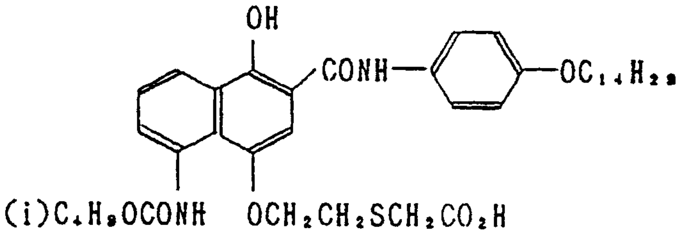
C－６７



C－６８



C－６９



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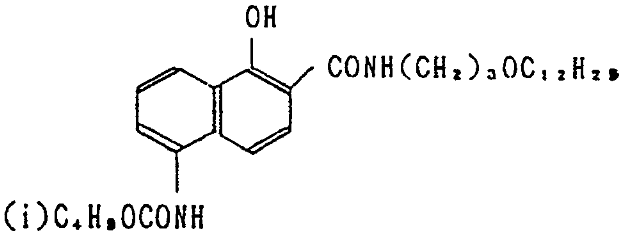
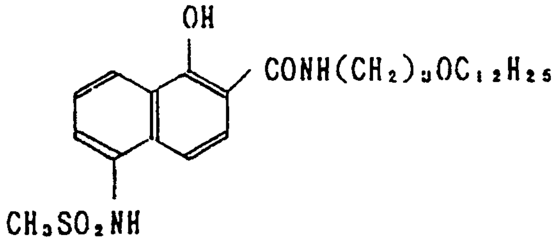
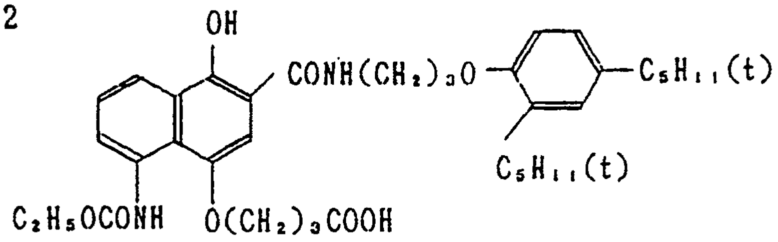


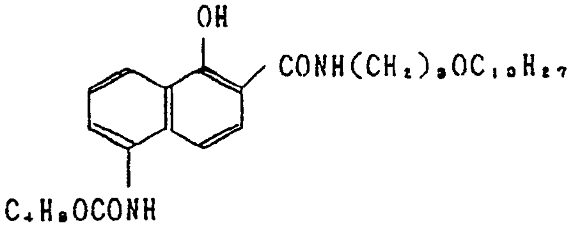
C－71



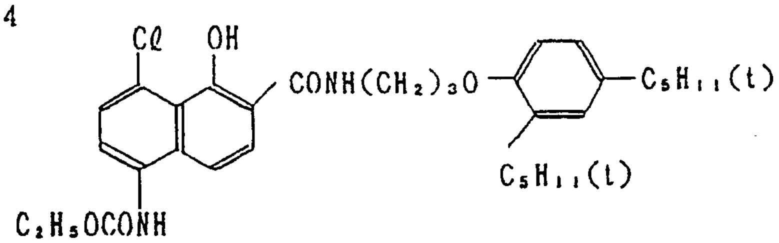
C－72



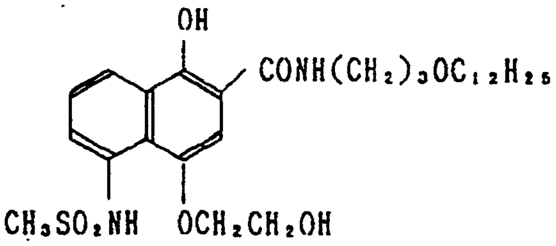
C－73



C－74



C－７５



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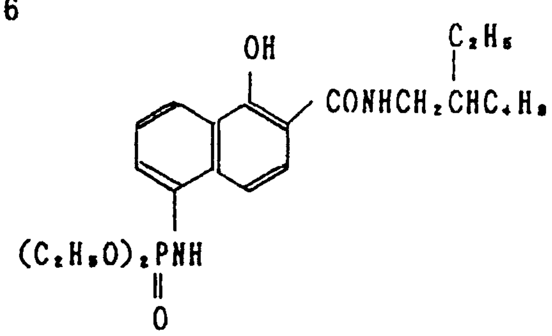

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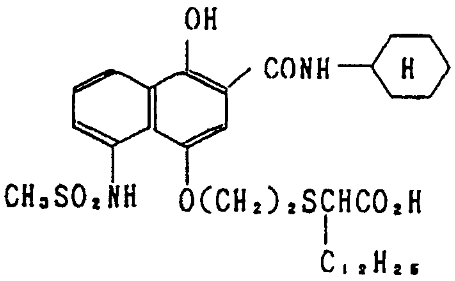
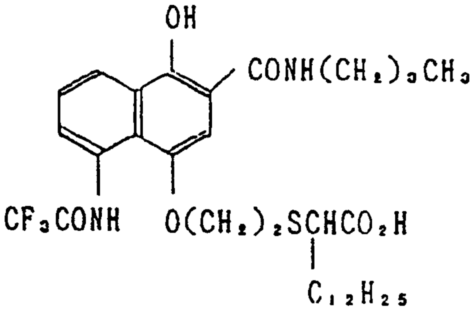
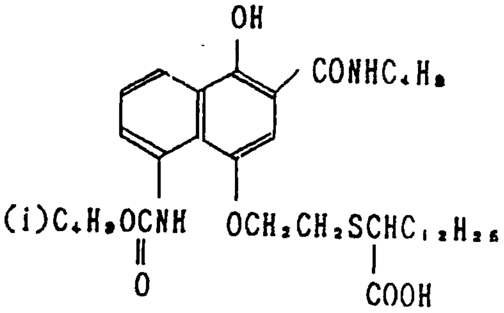


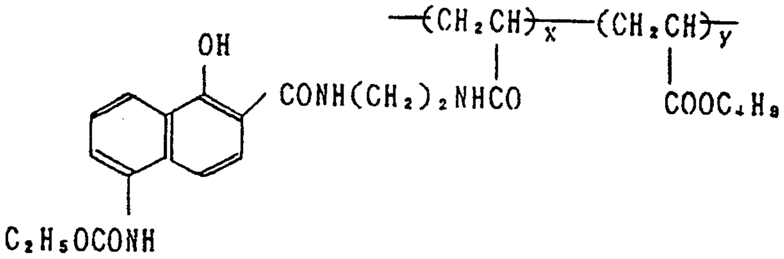
C－７８



C－79

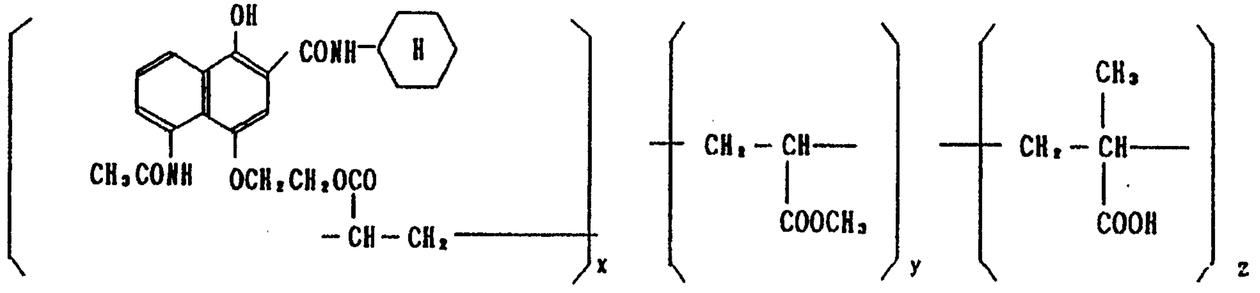


C－80



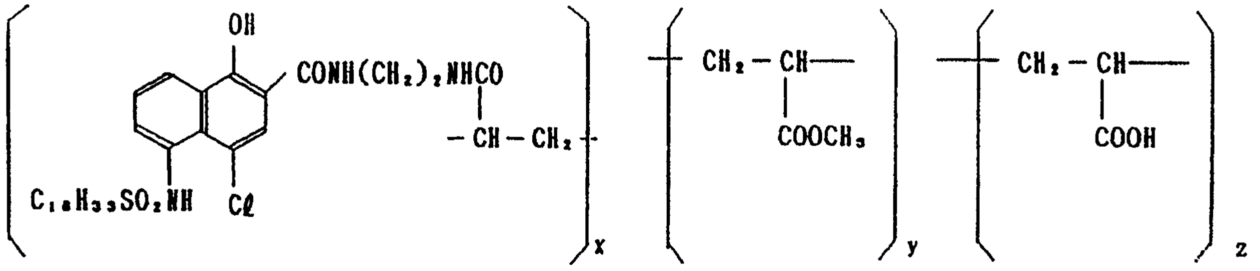
x : y = 60 : 40
(molar ratio)

C－81



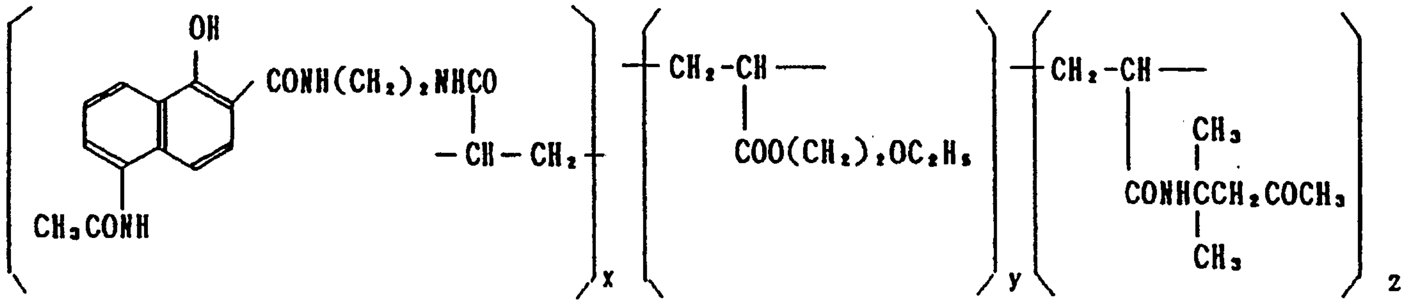
x : y : z = 5 : 4 : 1 (weight ratio)

C－82



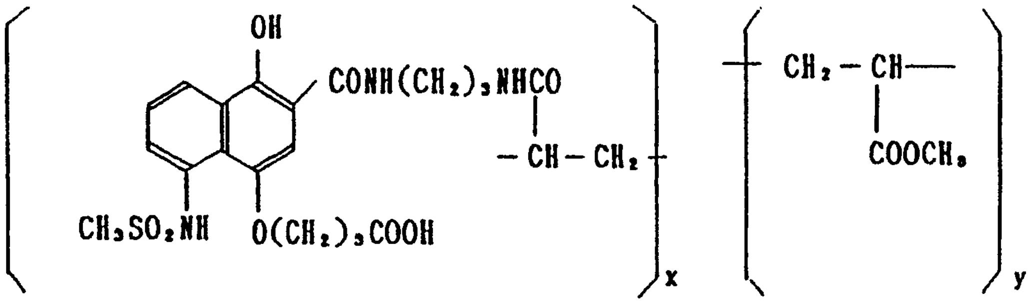
x : y : z = 67 : 26 : 7 (weight ratio)

C－83



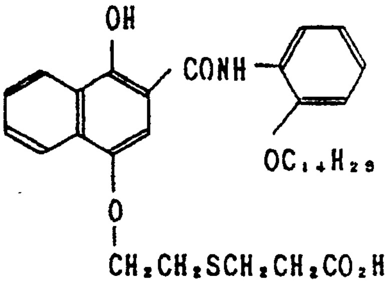
x : y : z = 2 : 1 : 1 (weight ratio)

C－84

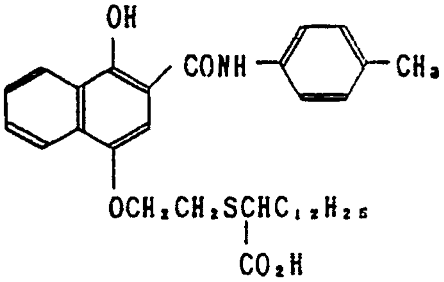


x : y = 1 : 4 (weight ratio)

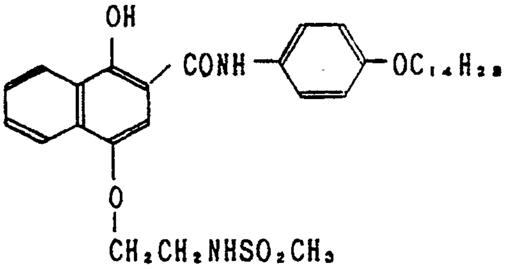
C－85



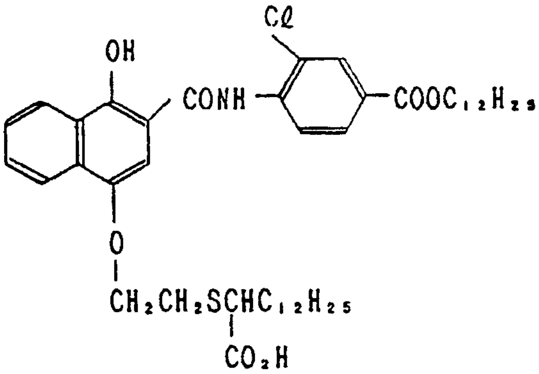
C－86



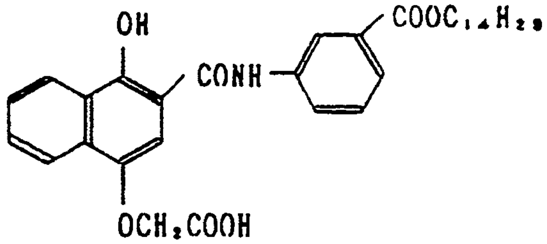
C－87



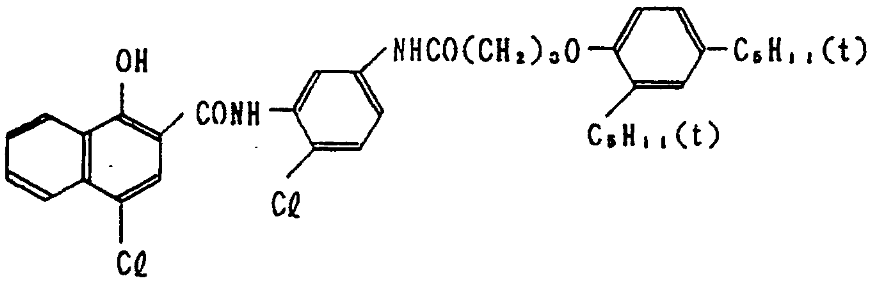
C－88



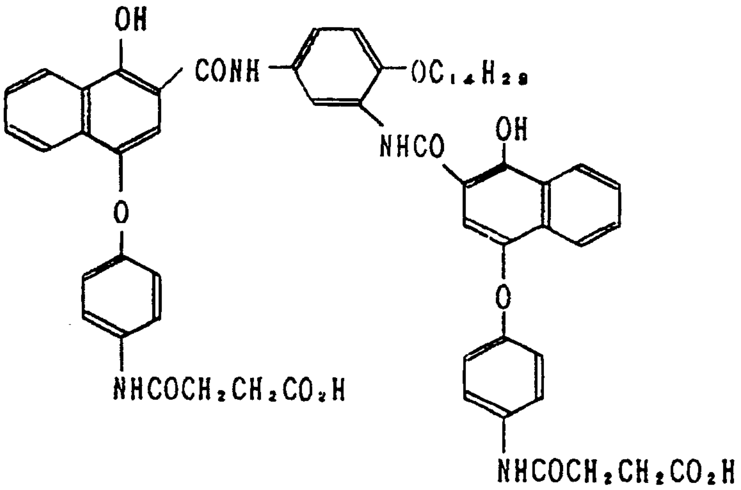
C－８９



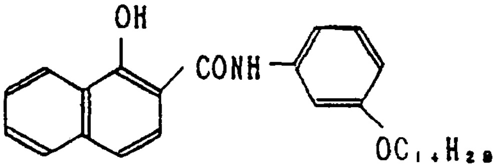
C－９０



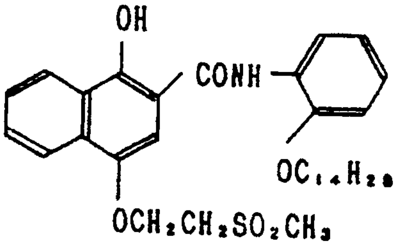
C－９１



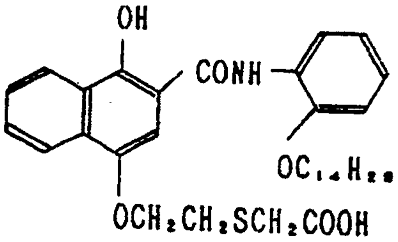
C－９２



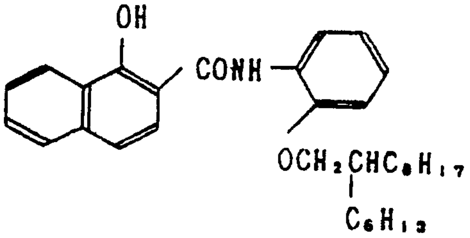
C－93



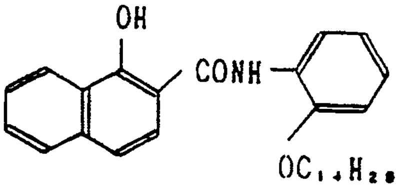
C－94



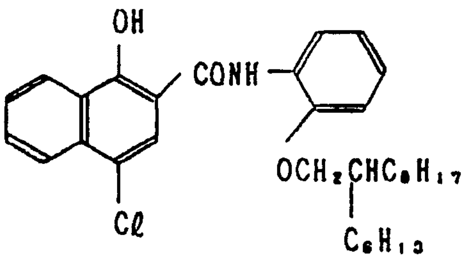
C－95



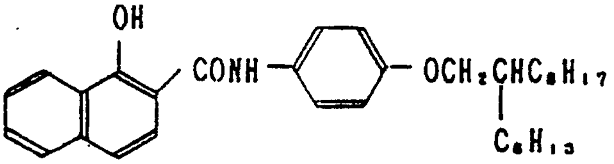
C－96



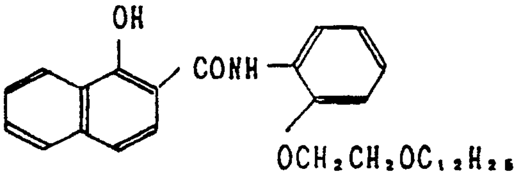
C－97



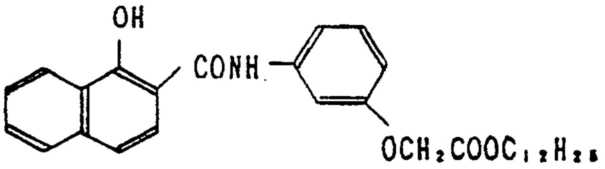
C－98



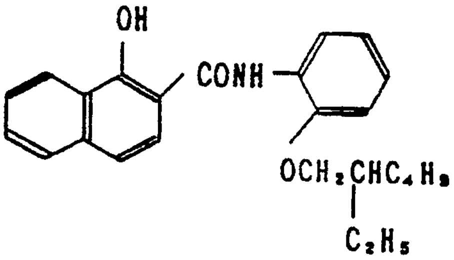
C－99



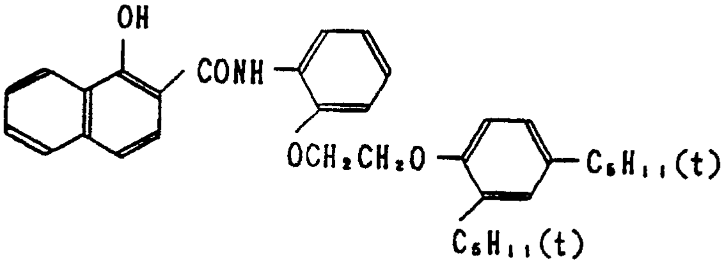
C－100



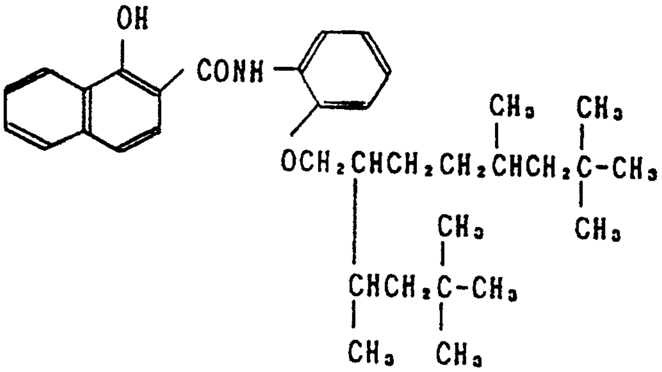
C - 101



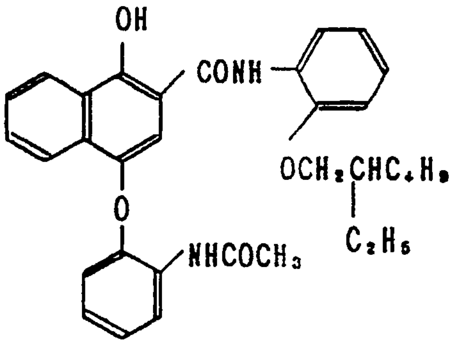
C - 102



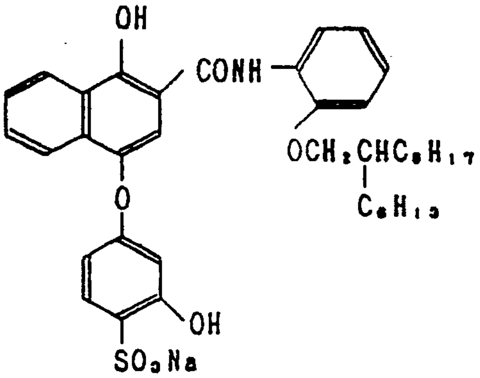
C - 103



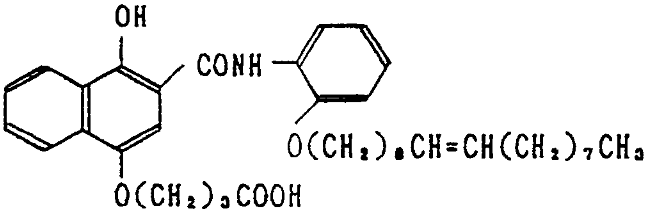
C − 104



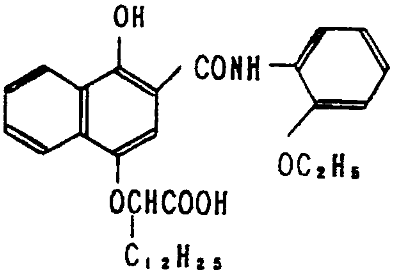
C − 105



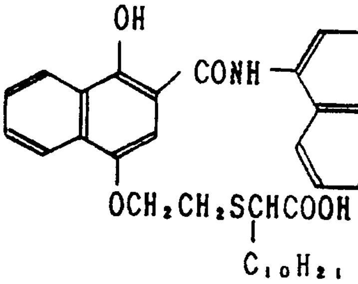
C − 106



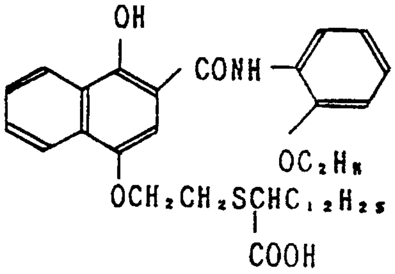
C − 107



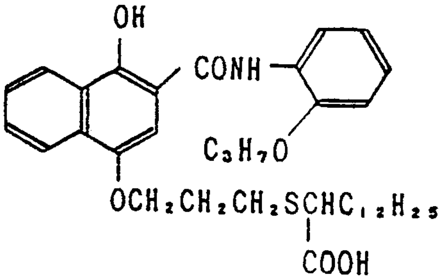
C − 108



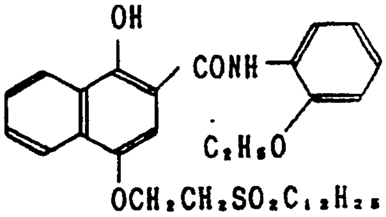
C − 109



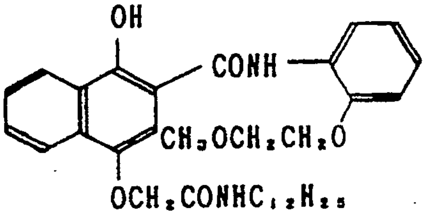
C − 110



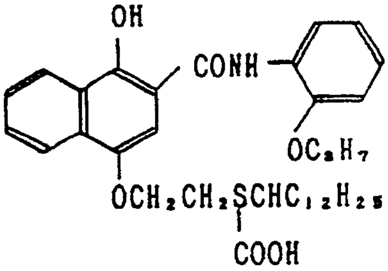
C - 111



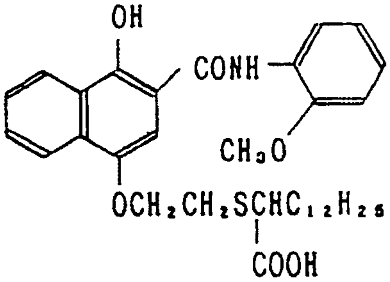
C - 112



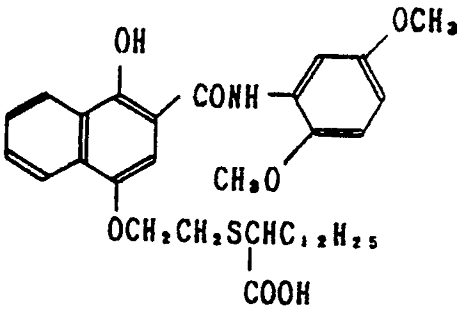
C - 113



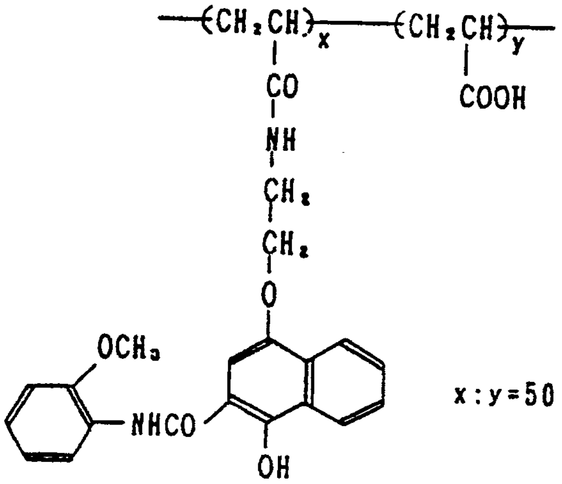
C - 114



C - 115

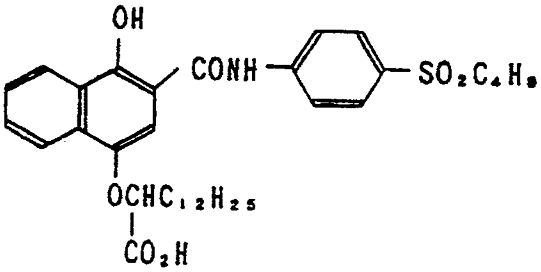


C - 116

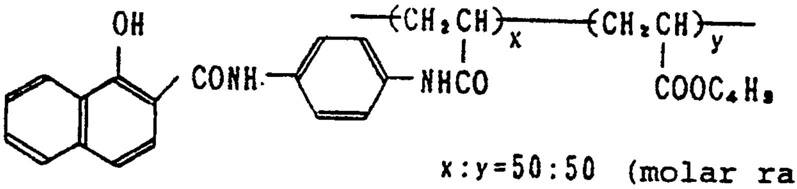


x:y=50:50 (molar ratio)

C - 117

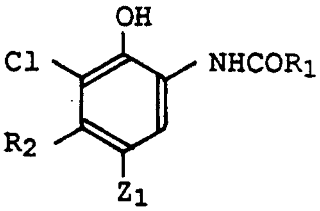


C - 118



x:y=50:50 (molar ratio)

When the light-sensitive color photographic material is a light-sensitive material for positive images (e.g. a color negative film), the preferred cyan coupler may include those represented by the following formula (C-1).



(C-1)

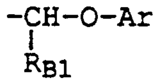
wherein R_1 represents a ballast group; R_2 represents an alkyl group having 2 or more carbon atoms; and Z_1 represents a hydrogen atom, or an atom or a group which can be eliminated by the reaction with an oxidized product of a color developing agent.

In the cyan coupler represented by the above formula (C-1), the alkyl group represented by R_2 may be straight or branched and include those having a substituent group.

R_2 is preferably an alkyl group having 2 to 6 carbon atoms.

The ballast group represented by R_1 is an organic group having a size and a shape which can give a volume sufficient to substantially prevent diffusion of a coupler from a layer in which the coupler is used to other layers, to a coupler molecule.

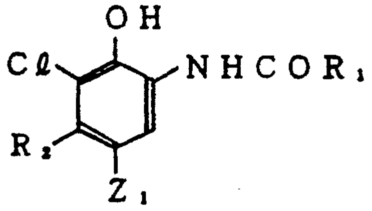
A preferred example of said ballast group is represented by the following formula.

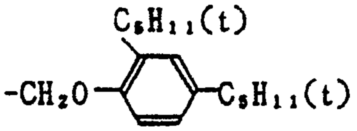
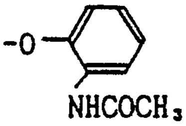
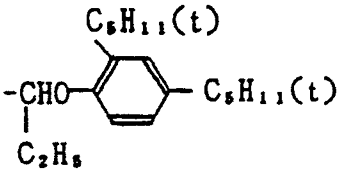
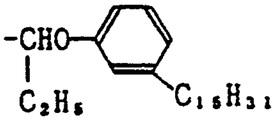
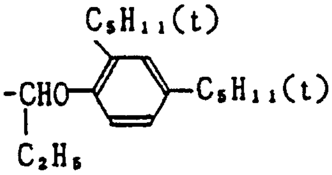


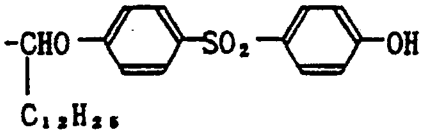
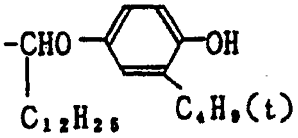
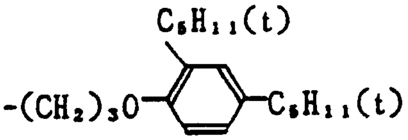
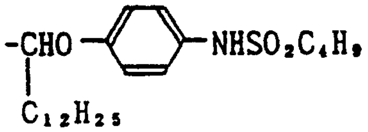
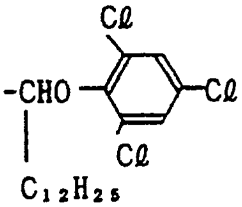
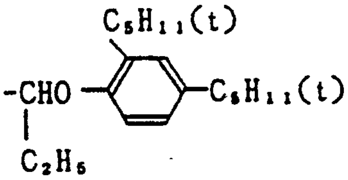
$$-\underset{\displaystyle R_{B1}}{\underset{|}{C}}H-O-Ar \qquad (C\text{-}1\text{-}A)$$

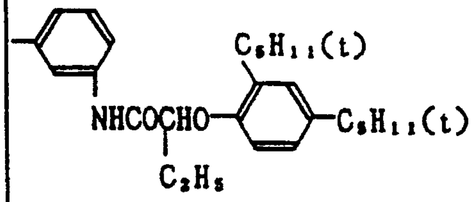
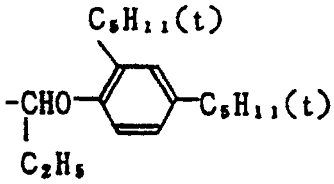
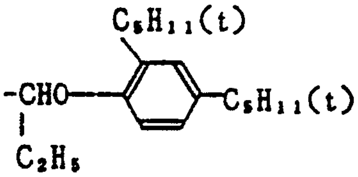
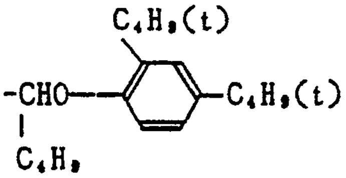
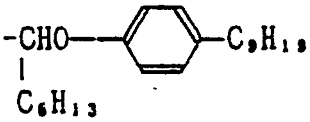
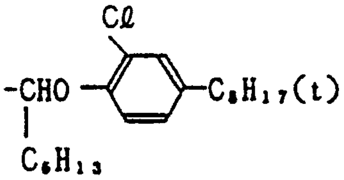
wherein R_{B1} represents an alkyl group having 1 to 12 carbon atoms; Ar represents an aryl group such as a phenyl group; and the aryl group includes those having a substituent groups.

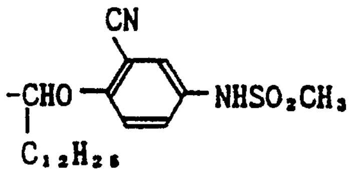
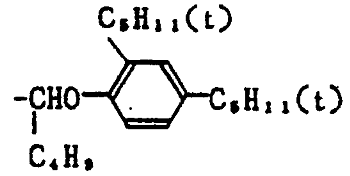
In the following, specific examples of the coupler represented by the formula (C-1) are shown, but the present invention is not limited to these.



Coupler No.	R_2	Z_1	R_1
C-1-1	$-C_2H_5$	$-C\ell$	
C-1-2	$-C_2H_5$		
C-1-3	$-C_3H_7(i)$	$-C\ell$	
C-1-4	$-C_2H_5$	$-C\ell$	

Coupler No.	R_2	Z_1	R_1
C-1-5	$-C_4H_9$	$-F$	
C-1-6	$-C_2H_5$	$-F$	
C-1-7	$-C_2H_5$	$-C\ell$	
C-1-8	$-C_2H_5$	$-C\ell$	
C-1-9	$-C_2H_5$	$-C\ell$	
C-1-10	$-C_6H_{13}$	$-C\ell$	

Coupler No.	R_2	Z_1	R_1
C-1-11	$-C_3H_7$	$-C\ell$	
C-1-12	$-(CH_2)_2-$* *$-NHCOCH_3$	$-C\ell$	
C-1-13	$-(CH_2)_2OCH_3$	$-C\ell$	
C-1-14	$-C_2H_5$	$-C\ell$	
C-1-15	$-C_4H_9(t)$	$-O(CH_2)_2-$* *$-SO_2CH_3$	
C-1-16	$-C_2H_5$	$-C\ell$	

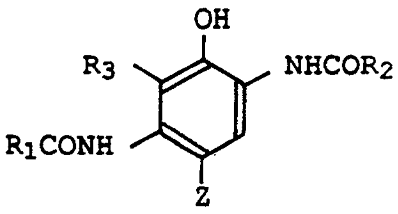
Coupler No.	R_2	Z_1	R_1
C-1-17	$-C_2H_5$	$-Cl$	
C-1-18	$-C_2H_5$	$-Cl$	

In addition to these examples, specific examples of the cyan coupler which can be used in the present invention are disclosed in Japanese Patent Publication No. 11572/1974, and Japanese Unexamined Patent Publications No. 3142/1986, No. 9652/1986, No. 9653/1986, No. 39045/1986, No. 50136/1986, No. 99141/1986 and No. 105545/1986.

The cyan dye-forming coupler represented by the above formula (C-1) of the present invention can be used generally in an amount of 1 x 10^{-3} mole to 1 mole, preferably in the range of 1 x 10^{-2} mole to 8 x 10^{-1} mole per mole of silver halide.

In the present invention, the cyan coupler represented by the formula (C-1) is preferably used in combination with a 2,5-diacylaminophenol type cyan coupler.

As the 2,5-diacylaminophenol type cyan coupler, a coupler represented by the following formula (C-2) is preferred.



(C-2)

wherein R_1 represents an alkyl group or an aryl group; R_2 represents an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; R_3 represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; R_3 may form a ring together with R_1; and Z represents a hydrogen atom, or an atom or a group which can be eliminated by reaction with an oxidized product of an aromatic primary amine type color developing agent.

In the cyan coupler represented by the above formula (C-2), the alkyl group represented by R_1 is preferably alkyl groups having 1 to 32 carbon atoms, and these alkyl groups may be straight or branched and also include those having a substituent group.

The aryl group represented by R_1 is preferably a phenyl group, and also includes those having a substituent group.

The alkyl group represented by R_2 is preferably alkyl groups having 1 to 32 carbon atoms, and these alkyl groups may be straight or branched and also include those having a substituent group.

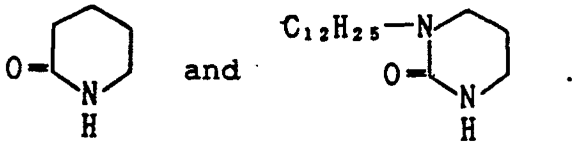
The cycloalkyl group represented by R_2 is preferably alkyl groups having 3 to 12 carbon atoms, and these cycloalkyl groups also include those having a substituent group.

The aryl group represented by R_2 is preferably a phenyl group, and also includes those having a substituent group.

The heterocyclic group represented by R_2 is preferably 5- to 7-membered heterocyclic groups, and these heterocyclic groups include those having a substituent group and may be fused.

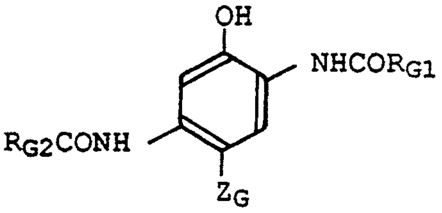
R_3 represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group, and said alkyl group and said alkoxy group may include those having a substituent group. However, R_3 is preferably a hydrogen atom.

The ring formed by R_1 and R_3 is preferably a 5- or 6-membered ring, and an example thereof may include



In the formula (I), an atom or a group represented by Z, which can be eliminated by reaction with an oxidized product of a color developing agent may include a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, a sulfonyloxy group, an acylamino group, a sulfonylamino group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group and an imide group (including those having a substituent group), but preferably a halogen atom, an aryloxy group and an alkoxy group.

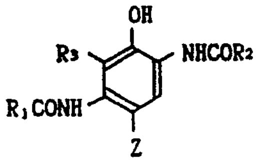
Among the above cyan couplers, particularly preferred are a cyan coupler represented by the following formula (C-2A).

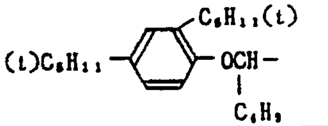
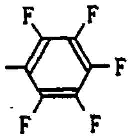
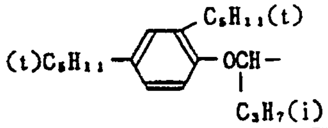
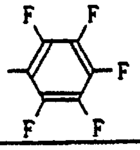
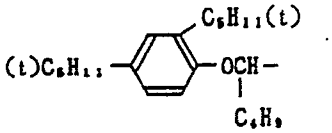
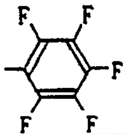
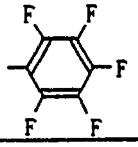
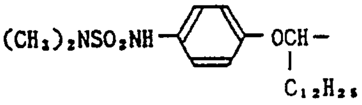
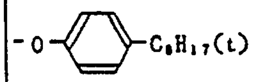
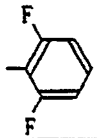
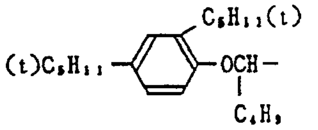
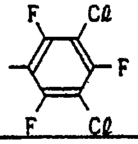
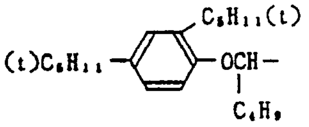
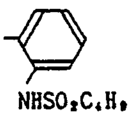
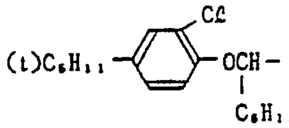
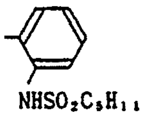
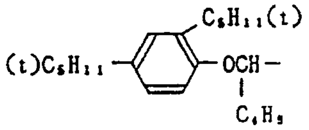
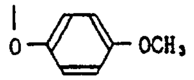


(C-2A)

wherein R_{G1} represent a phenyl group substituted with at least one halogen atom and further includes those having a substituent group other than a halogen atom; R_{G2} has the same meaning of R_1 in the above formula (C-2); and Z_G represents a halogen atom, an aryloxy group or an alkoxy group and includes those having a substituent group.

In the following, representative specific examples of the cyan couplers represented by the formula (C-2) are shown.



Exemplary compound No.	R_2	R_1	R_3	Z
C−2−1	$-(CF_2)_4H$		H	−Cℓ
C−2−2			H	−Cℓ
C−2−3			H	−Cℓ
C−2−4		$C_{16}H_{33}-$	-Cℓ	−Cℓ
C−2−5			H	
C−2−6			H	H
C−2−7			H	−Cℓ
C−2−8			H	−Cℓ
C−2−9			H	

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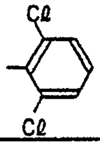
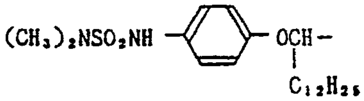
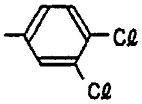
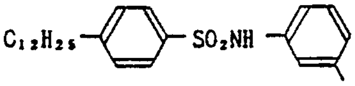
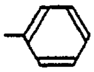
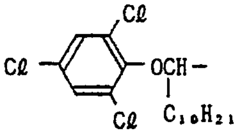
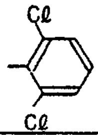
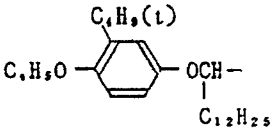
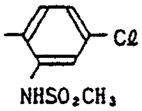
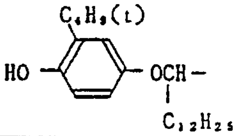
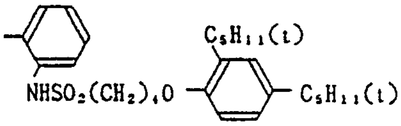
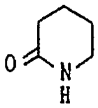
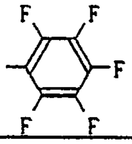
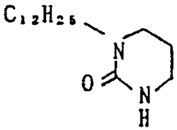
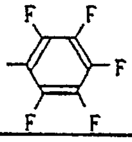
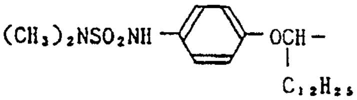
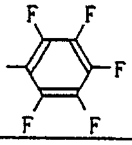
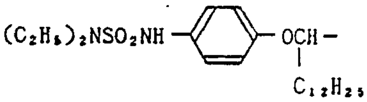
<tr><td>C−2−10</td><td> </td><td> </td><td>H</td><td>−Cℓ</td></tr>
<tr><td>C−2−11</td><td> </td><td> </td><td>H</td><td>−Cℓ</td></tr>
<tr><td>C−2−12</td><td></td><td> </td><td>H</td><td>$-OCH_2CONHC_3H_7$</td></tr>
<tr><td>C−2−13</td><td> </td><td> </td><td>H</td><td>−Cℓ</td></tr>
<tr><td>C−2−14</td><td> </td><td> </td><td>H</td><td>−Cℓ</td></tr>
<tr><td>C−2−15</td><td colspan="2"> </td><td> </td><td>−Cℓ</td></tr>
<tr><td>C−2−16</td><td> </td><td colspan="2"> </td><td>−Cℓ</td></tr>
<tr><td>C−2−17</td><td> </td><td> </td><td>H</td><td>−Cℓ</td></tr>
<tr><td>C−2−18</td><td> </td><td> </td><td>H</td><td>−Cℓ</td></tr>
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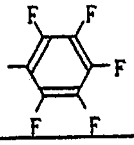
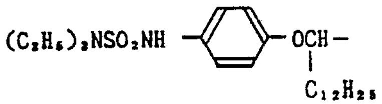
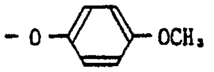
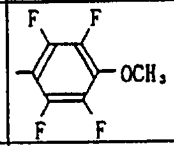
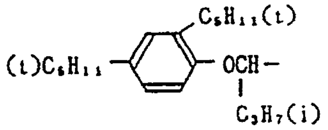
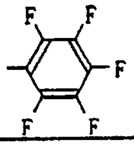
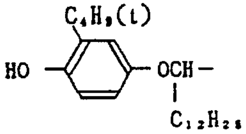
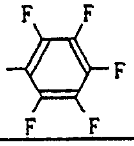
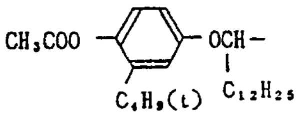
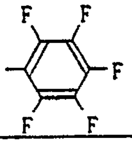
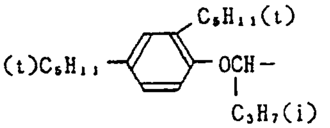
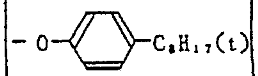
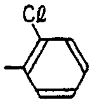
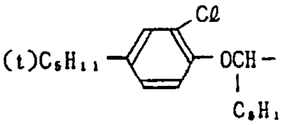
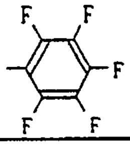
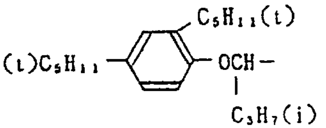
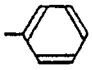
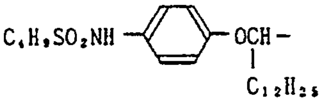
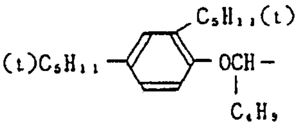
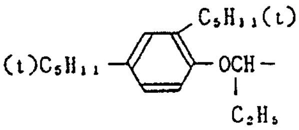
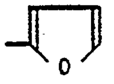
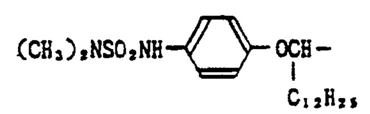
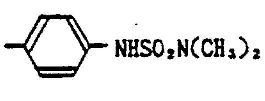
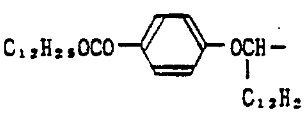
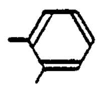
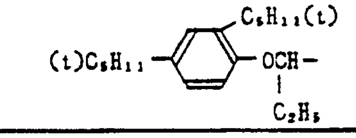
C－2－19			H	
C－2－20			H	－Cℓ
C－2－21			H	－Cℓ
C－2－22			H	－Cℓ
C－2－23			H	
C－2－24			H	－Cℓ
C－2－25			H	$-OCH_2CONH(CH_2)_2OCH_3$
C－2－26			H	－Cℓ
C－2－27	$-C_3F_7$		H	H
C－2－28	$-C_3F_7$		H	H

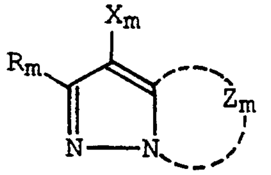
Exemplary compound No.	R_2	R_1	R_3	Z
C-2-29			H	Cl
C-2-30			CH_3O	Cl
C-2-31			H	Cl

As a specific example of the above cyan coupler, there may be further included, for example, 2,5-diacylamino type cyan couplers disclosed on pp. 26 to 35 of Japanese Unexamined Patent Publication No. 178962/1987, in the left lower column on p. 7 to the right lower column on p. 10 of Japanese Unexamined Patent Publication No. 225155/1985, in the left upper column on p. 6 to the right lower column on p. 8 of Japanese Unexamined Patent Publication No. 222853/1985 and in the left lower column on p. 6 to the left upper column on p. 9 of Japanese Unexamined Patent Publication No. 185335/1984, and these couplers can be synthesized according to the methods disclosed in these publications.

The cyan dye-forming coupler represented by the above formula (C-2) of the present invention can be used generally in an amount of 1 x 10^{-3} to 1 mole, preferably in the range of 1 x 10^{-2} mole to 8 x 10^{-1} mole per mole of silver halide.

When the cyan coupler represented by the above formula (C-1) and the cyan coupler represented by the formula (C-2) are used in combination, their mixing ratio is preferably 1 : 9 to 9 : 1, particularly preferably 7 : 3 to 3 : 7 in terms of a molar ratio.

Next, the magenta coupler preferably used in the present invention is represented by the following formula (M-I).



(M-I)

In the formula (M-I), Z_m represents a group of non-metallic atoms necessary for forming a nitrogen-containing heterocyclic ring, and the ring formed by said Z_m may have a substituent group.

X_m represents a hydrogen atom or a group which can be eliminated by reaction with an oxidized product of a color developing agent.

The substituent group represented by R_m is not particularly limited, but may representatively include each group of alkyl, aryl, anilino, acylamino, sulfonamide, alkylthio, arylthio, alkenyl and cycloalkenyl. Additionally, there may be mentioned a halogen atom, and each group of cycloalkenyl, alkynyl, hetero ring, sulfonyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imide, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkoxycarbonyl, aryloxycarbonyl and heterocyclic thio, and also a spiro-compound residue and a bridged hydrocarbon compound residue.

The alkyl group represented by R_m are preferably alkyl groups having 1 to 32 carbon atoms, which may be straight or branched.

The aryl group represented by R_m is preferably a phenyl group.

The acylamino group represented by R_m may include an alkylcarbonylamino group and an arylcarbonylamino group.

The sulfonamide group represented by R_m may include, for example, an alkylsulfonylamino group and an arylsulfonylamino group.

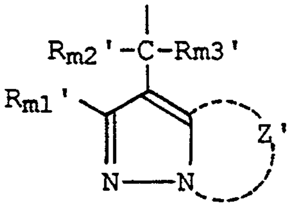
The alkyl component and aryl component in the alkylthio group and arylthio group represented by R_m are each the alkyl group and aryl group represented by the above R_m.

The alkenyl group represented by R_m is alkenyl groups having 2 to 32 carbon atoms, and the cycloalkyl group is cycloalkyl groups preferably having 3 to 12 carbon atoms, particularly preferably 5 to 7 carbon atoms. The alkenyl groups may be straight or branched.

The cycloalkenyl group represented by R_m is cycloalkenyl groups preferably having 3 to 12 carbon atoms, particularly preferably 5 to 7 carbon atoms.

The sulfonyl group represented by R_m may include an alkylsulfonyl group and an arylsulfonyl group; the sulfinyl group, for example, an alkylsulfinyl group and arylsulfinyl group; the phosphonyl group, for example, an alkylphosphonyl group, an alkoxyphosphonyl group, an aryloxyphosphonyl group and an arylphosphonyl group; the acyl group, for example, an alkylcarbonyl group and an arylcarbonyl group; the carbamoyl group, for example, an alkylcarbamoyl group and an arylcarbamoyl group; the sulfamoyl group, for example, an alkylsulfamoyl group and an arylsulfamoyl group; the acyloxy group, for example, an alkylcarbonyloxy group and an arylcarbonyloxy group; the carbamoyloxy group, for example, an alkylcarbamoyloxy group and an arylcarbamoyloxy group; the ureido group, for example, an alkylureido group and an arylureido group; the sulfamoylamino group, for example, an alkylsulfamoylamino group and an arylsulfamoylamino group; the heterocyclic group, preferably 5- to 7-membered cyclic groups, specifically including a 2-furyl group, a 2-thienyl group, a 2-pyrimidinyl group and a 2-benzothiazolyl group; the heterocyclic oxy group, preferably groups having 5- to 7-membered heterocyclic rings, specifically including a 3,4,5,6-tetrahydropyranyl-2-oxy group, a 1-phenyltetrazole-5-oxy group; the heterocyclic thio group, preferably 5- to 7-membered heterocyclic thio groups, for example, a 2-pyridylthio group, a 2-benzothiazolylthio group, a 2,4-diphenoxy-1,3,5-triazole-6-thio group; the siloxy group, a triethylsiloxy group, a triethylsiloxy group and a dimethybutylsiloxy group; the imide group, a succinimide group, a 3-heptadecyl succinimide group, a phthalimide group and a glutarimide group; the spiro-compound residue, spiro[3,3]-heptan-1-yl; the bridged hydrocarbon compound residue, bicyclo[2.2.1]heptan-1-yl, tricyclo[3.3.1.1^{3,7}]-decan-1-yl and 7,7-dimethyl-bicyclo[2.2.1]heptan-1-yl.

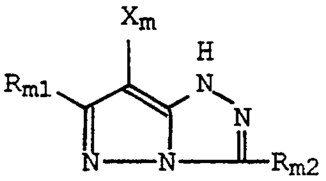
The group represented by X_m, which can be eliminated by reaction with an oxidized product of a color developing agent, may include, for example, a halogen atom (a chlorine atom, a bromine atom and a fluorine atom), and each group of alkoxy, aryloxy, heterocyclic oxy, acyloxy, sulfonyloxy, alkoxycarbonyloxy, aryloxycarbonyl, alkyloxalyloxy, alkoxyoxalyloxy, alkylthio, arylthio, heterocyclic thio, alkyloxycarbonylthio, acylamino, sulfonamide, nitrogen-containing hetero ring which is bonded by N atom, alkyloxycarbonylamino, aryloxycarbonylamino, carboxyl, and

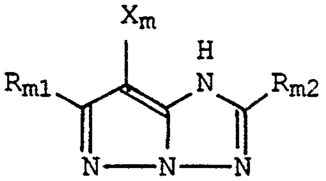


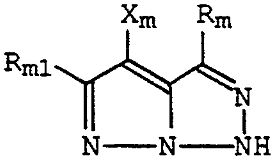
wherein $R_{m1'}$ has the same meaning as the above R_m; Z' has the same meaning as the above Z; and $R_{m2'}$ and $R_{m3'}$ each represent a hydrogen atom, an aryl group, an alkyl group or a heterocyclic ring, preferably a halogen atom, particularly preferably a chlorine atom.

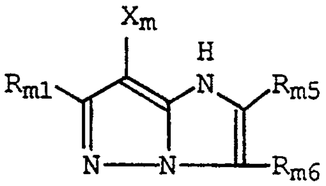
Further, the nitrogen-containing hetero ring formed by Z_m or Z' may include, for example, a pyrazole ring, an imidazole ring, a triazole ring or a tetrazole ring, and as a substituent group which may be possessed by the above rings, there may be mentioned those in the description of the above R_m.

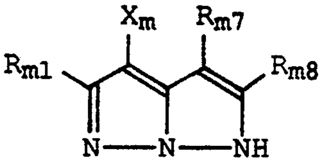
Those represented by the formula (M-I) are further specifically represented by, for example, the following formulae (M-II) to (M-VII).

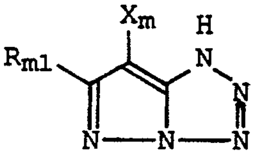

(M-II)


(M-III)


(M-IV)

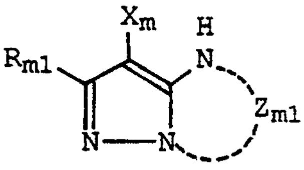

(M-V)


(M-VI)


(M-VII)

In the above formulae (M-II) to (M-VII), R_{m1} to R_{m8} and X_m each have the same meaning as the above R_m and X_m.

Among the magenta couplers represented by the formula (M-I), preferred is a magenta coupler represented by the following formula (M-VIII).


(M-VIII)

wherein R_{m1}, X_m and Z_{m1} each have the same meanings as R_{m1}, X_m and Z_m in the formula (M-I).

Among the magenta couplers represented by the above formulae (M-II) to (M-VII), particularly preferred is the magenta coupler represented by the formula (M-II).

The substituent groups which may be possessed by the ring formed by Z_m in the formula (M-I) and the ring formed by Z_{m1} in the formula (M-VIII), and R_{m2} to R_{m8} in the formulae (M-II) to (M-VI) are preferably those represented by the following formula (M-IX).

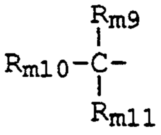
$-R^{m1}-SO_2-R^{m2}$ (M-IX)

wherein R^{m1} represents an alkylene group; and R^{m2} represents an alkyl group, a cycloalkyl group or an aryl group.

The alkylene group represented by the above R^{m1} may have preferably 2 or more, more preferably 3 to 6 carbon atoms in its straight portion, and may be either straight or branched.

The cycloalkyl group represented by the above R^{m2} is preferably 5- or 6-membered.

When used for forming positive images, most preferred substituent groups R_m and R_{m1} on the above hetero ring are represented by the following formula (M-X).



$$R_{m10}-\overset{\displaystyle R_{m9}}{\underset{\displaystyle R_{m11}}{\overset{|}{\underset{|}{C}}}}- \qquad \text{(M-X)}$$

wherein R_{m9}, R_{m10} and R_{m11} each have the same meaning of the above R_m.

Two of R_{m9}, R_{m10} and R_{m11}, for example, R_{m9} and R_{m10} may be bonded to form a saturated or unsaturated ring (e.g. cycloalkane, cycloalkene and hetero ring), and further, R_{m11} may be bonded to said ring to constitute a bridged hydrocarbon compound residue.

Among those represented by the formula (M-X), preferred are the case (i) where at least two of R_{m9} to R_{m11} are alkyl groups, and the case (ii) where one of R_{m9} to R_{m11}, for example, R_{m11} is a hydrogen atom, and the other two of R_{m9} and R_{m10} are bonded to form cycloalkyl together with a root carbon atom.

In the case (i), preferred is the case where two of R_{m9} to R_{m11} are alkyl groups, and the other one is a hydrogen atom or an alkyl group.

Further, when used for forming negative images, most preferred substituent groups R_m and R_{m1} on the above hetero ring are represented by the following formula (M-XI).

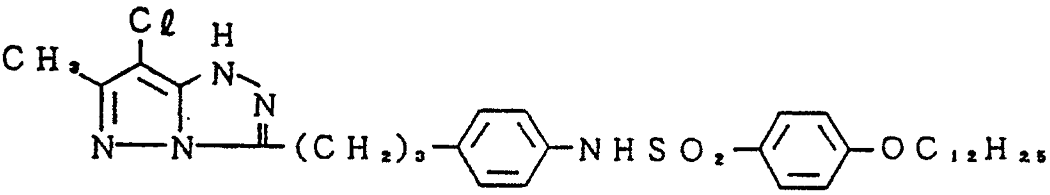
$R_{m12}-CH_2-$ (XI)

wherein R_{m12} has the same meaning of the above R_m.

R_{m12} is preferably a hydrogen atom or an alkyl group.

In the following, representative specific examples of the compound represented by the formula (M-I) are shown.

M-1



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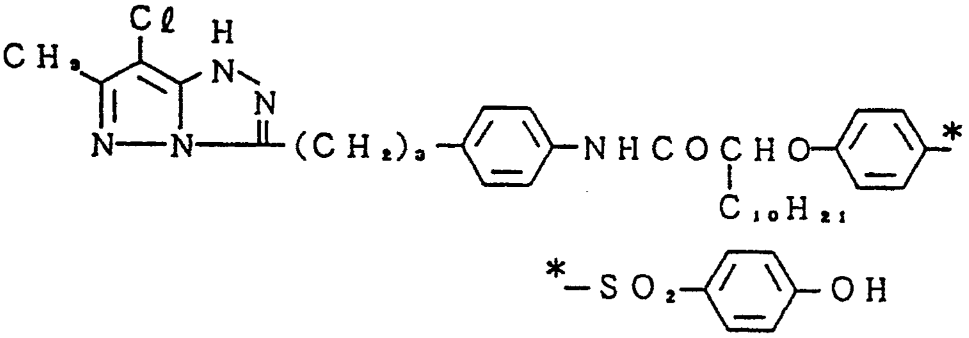

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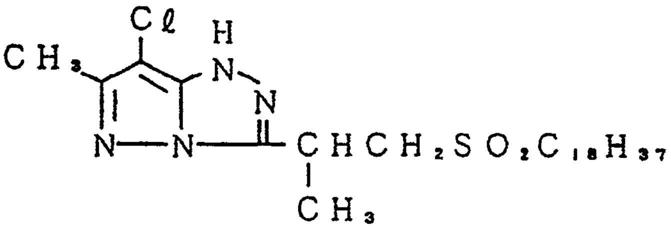

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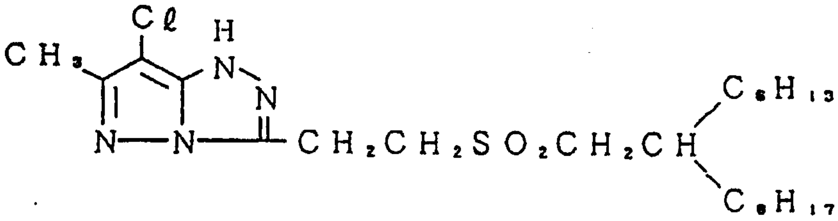

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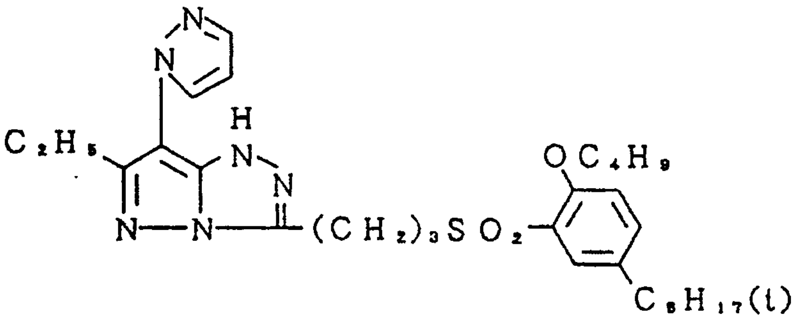

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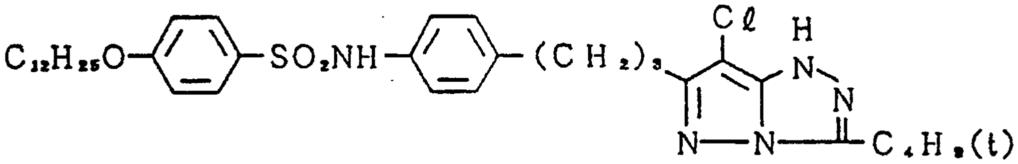

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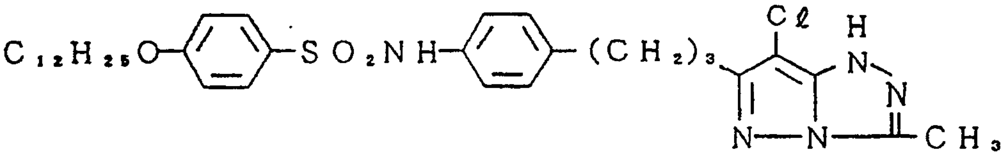

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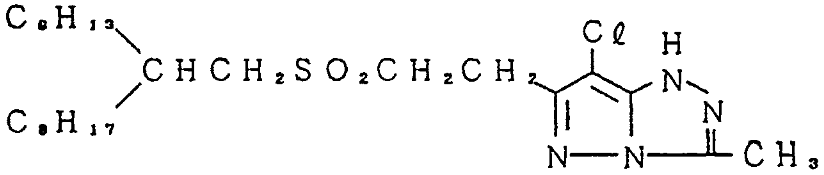

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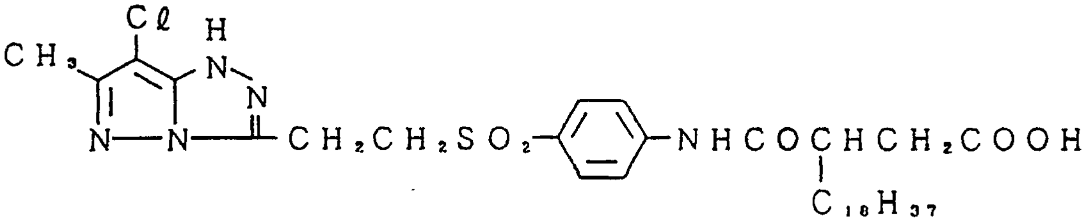

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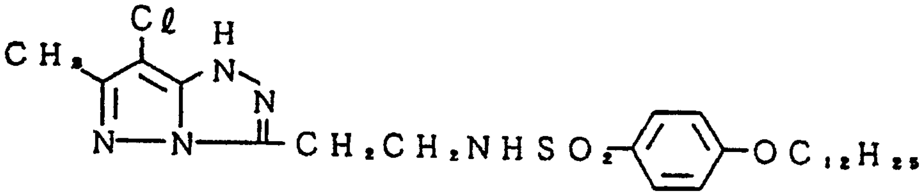

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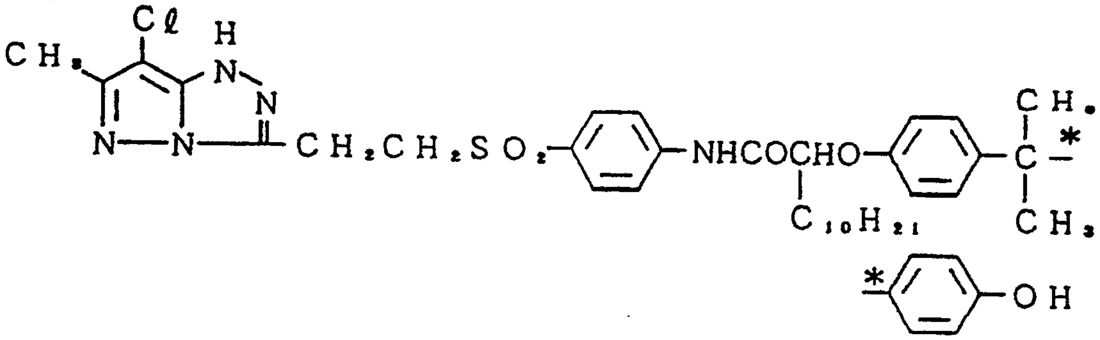

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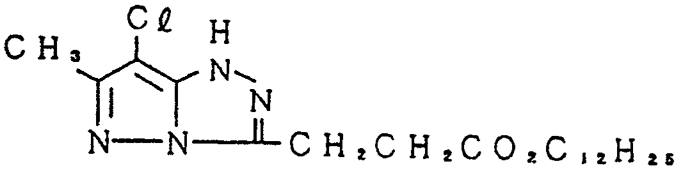

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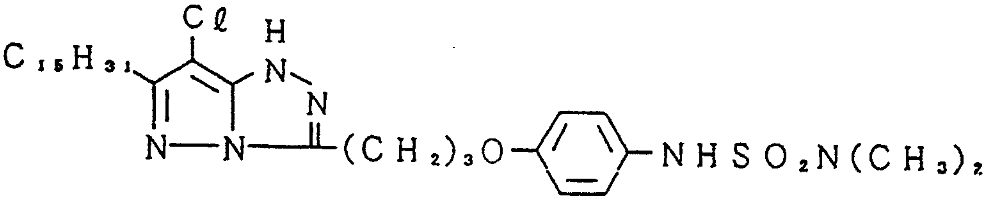

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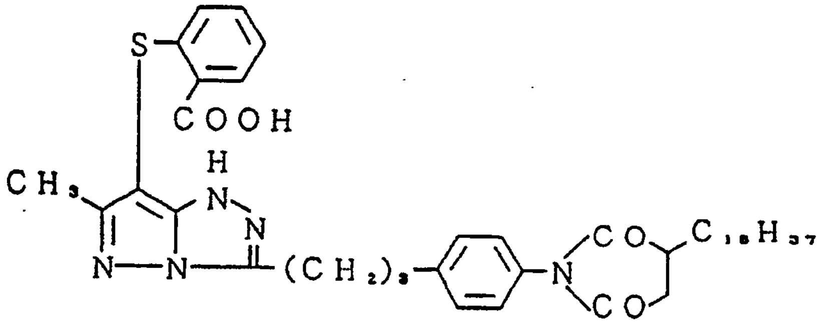

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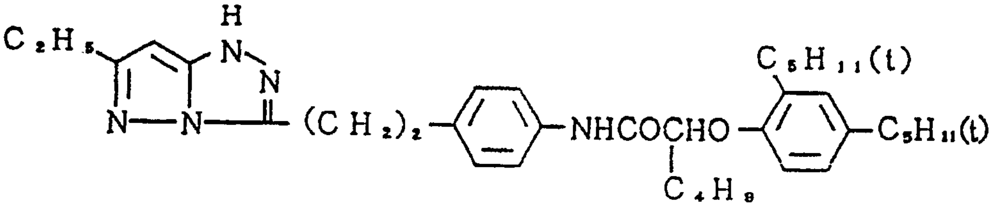

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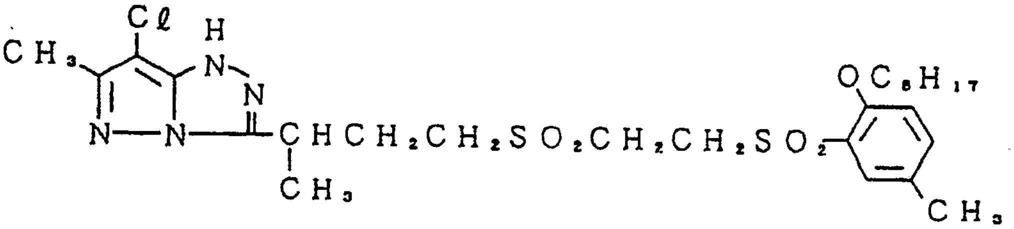

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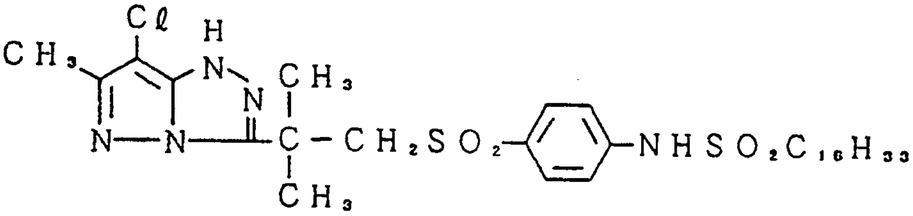

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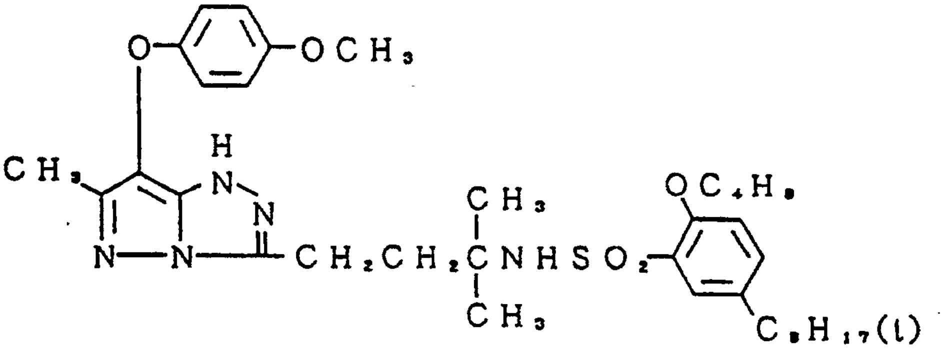

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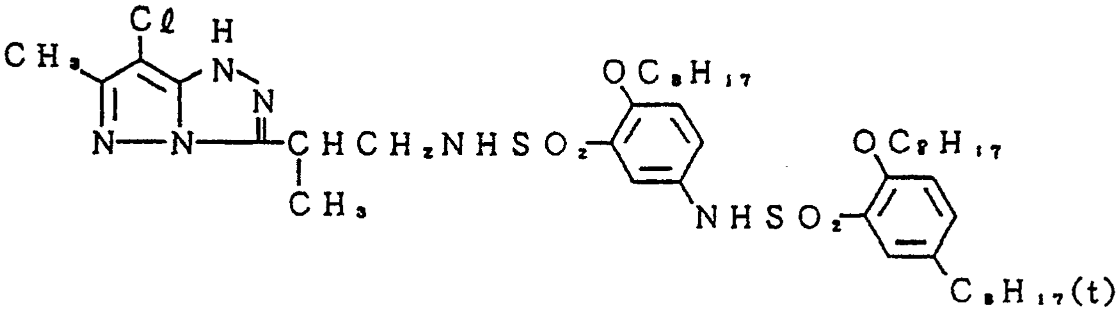

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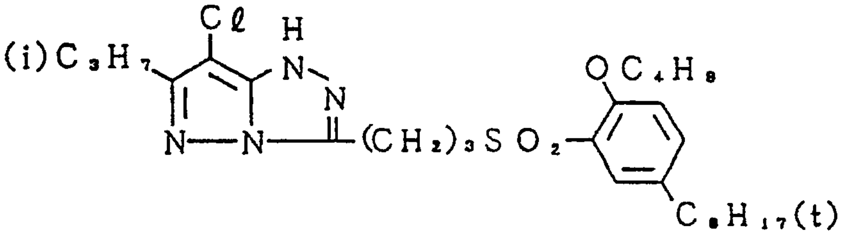

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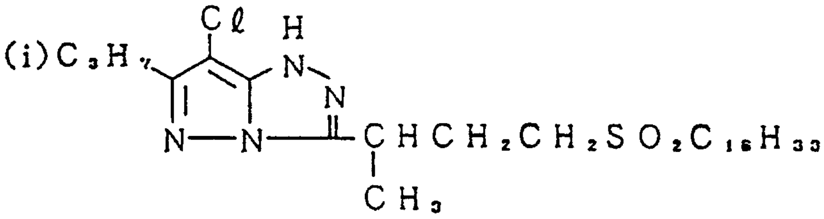

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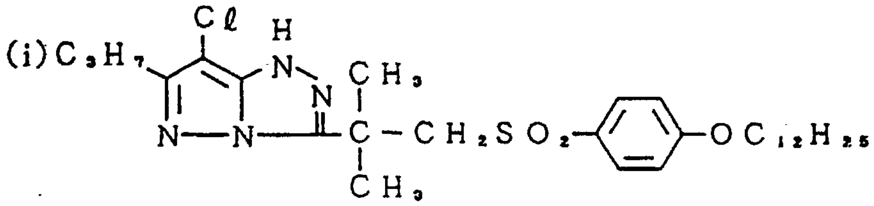

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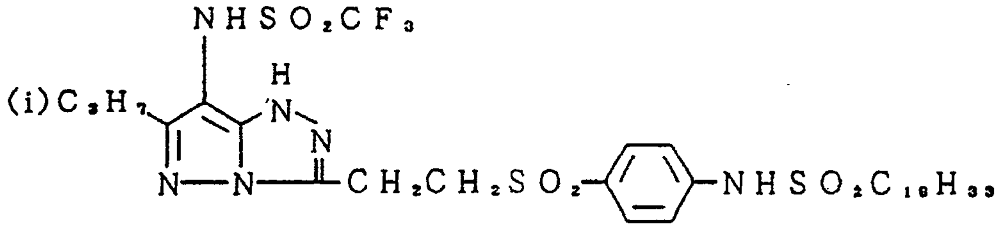

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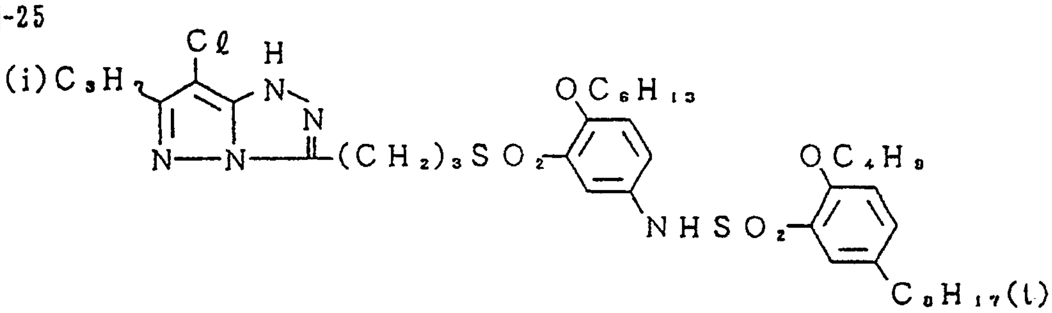

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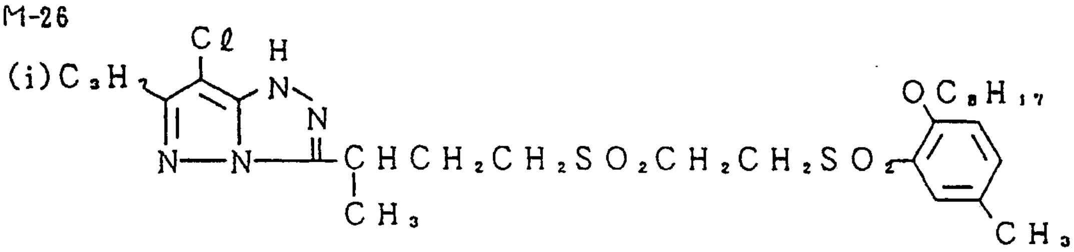

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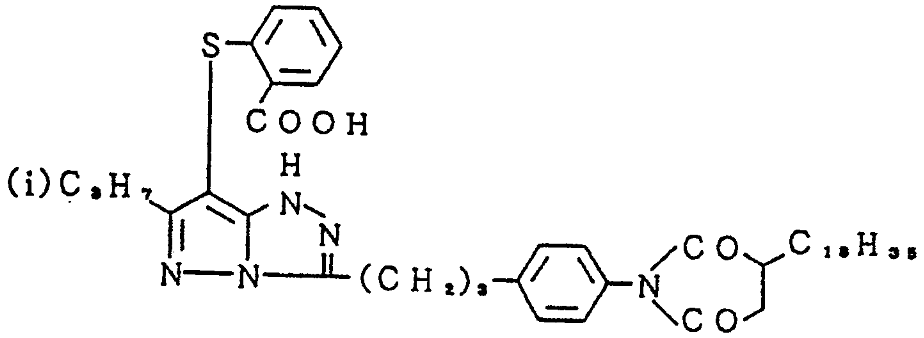

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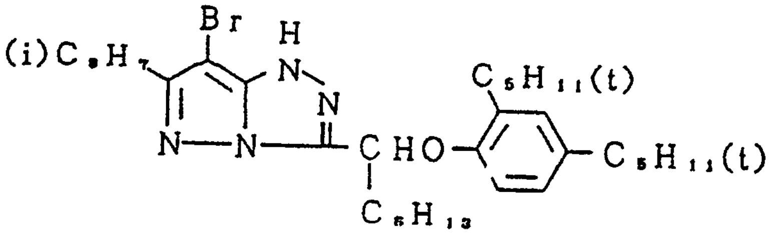

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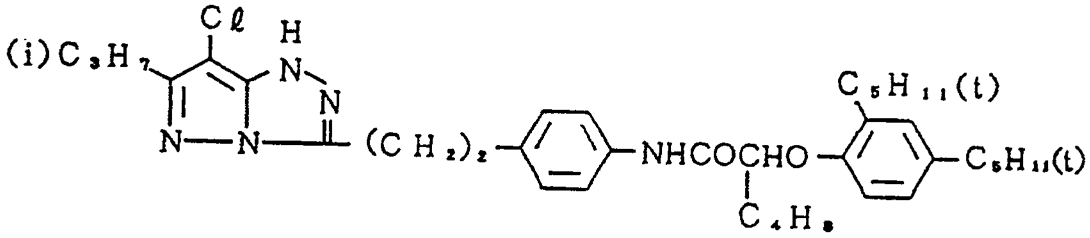

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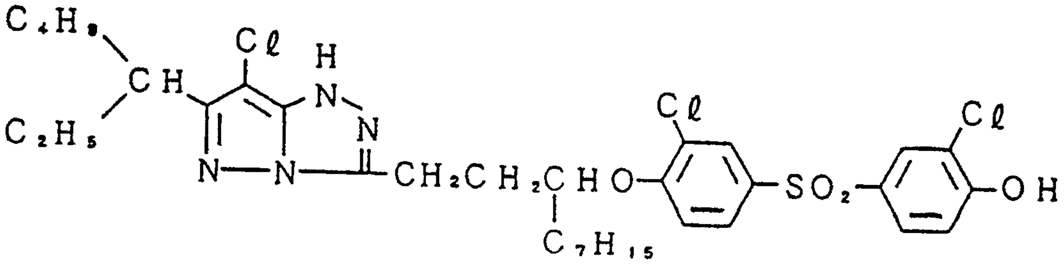

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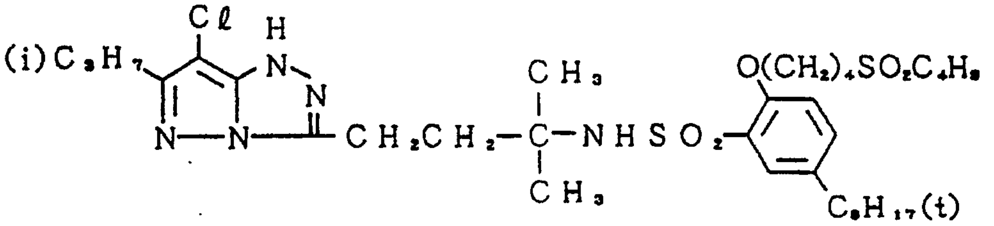

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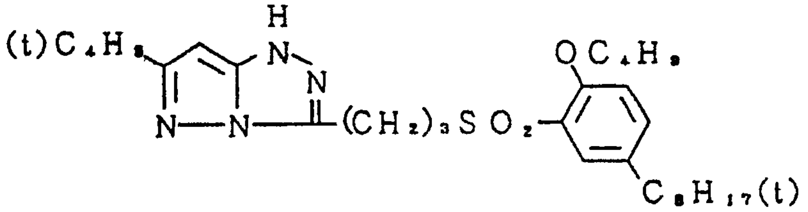

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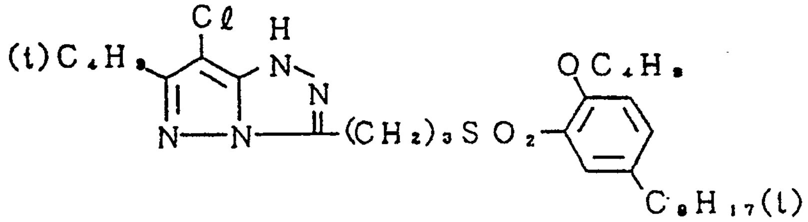

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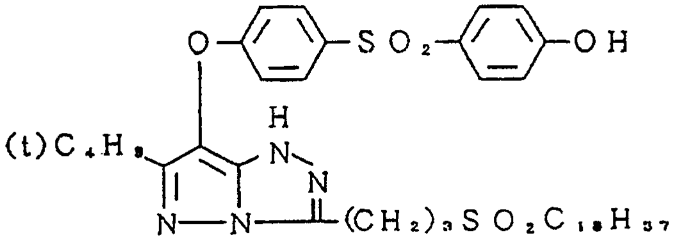

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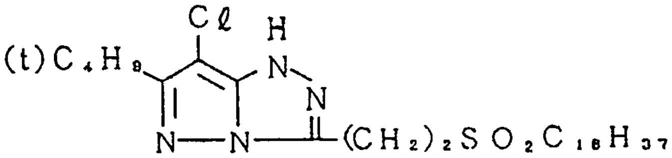

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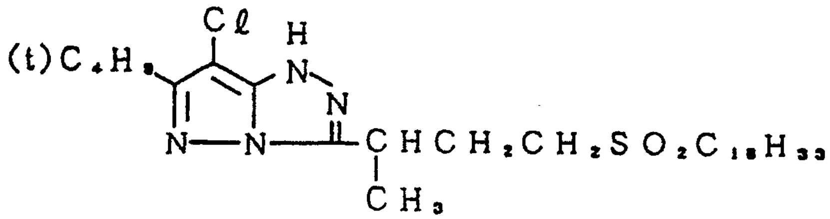

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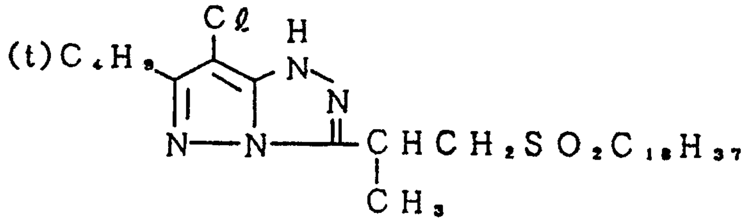

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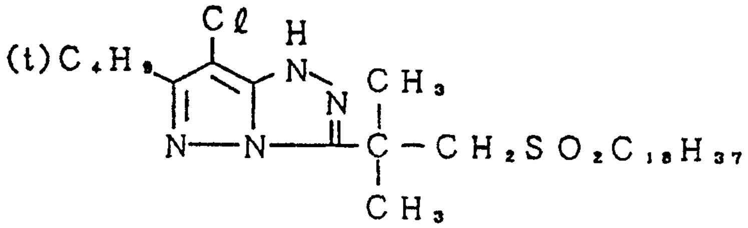

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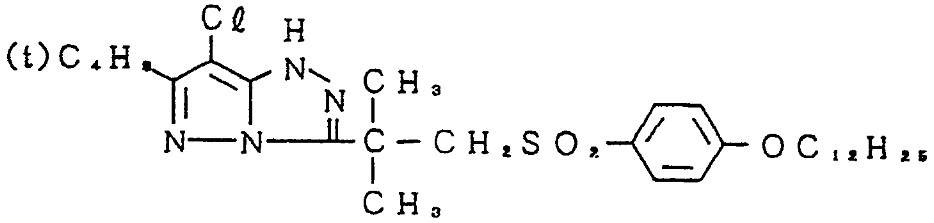

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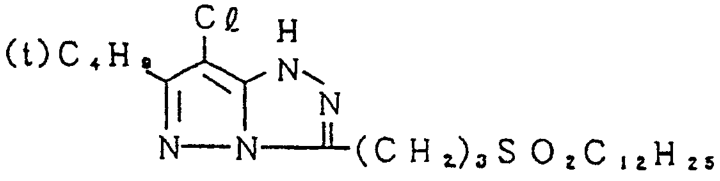

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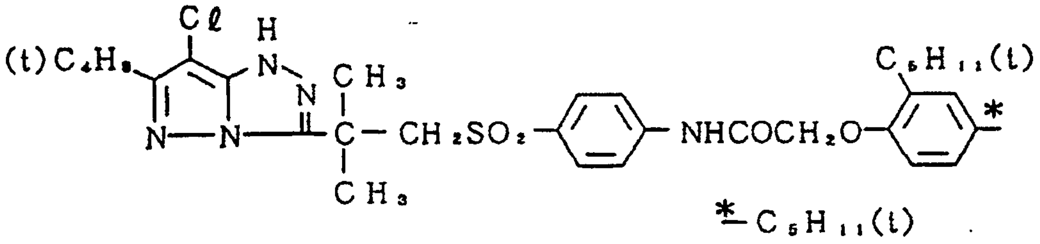

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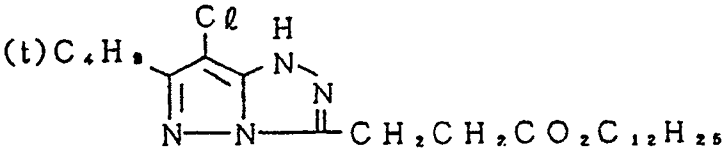

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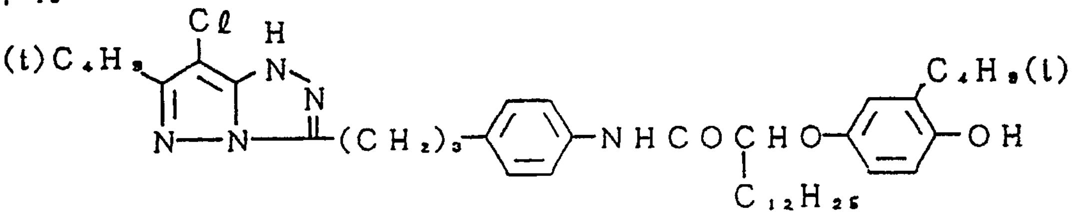

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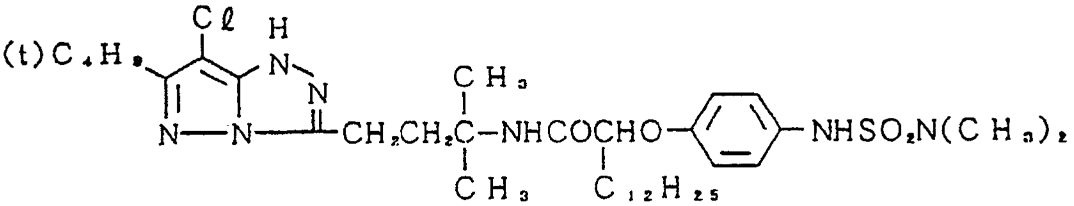

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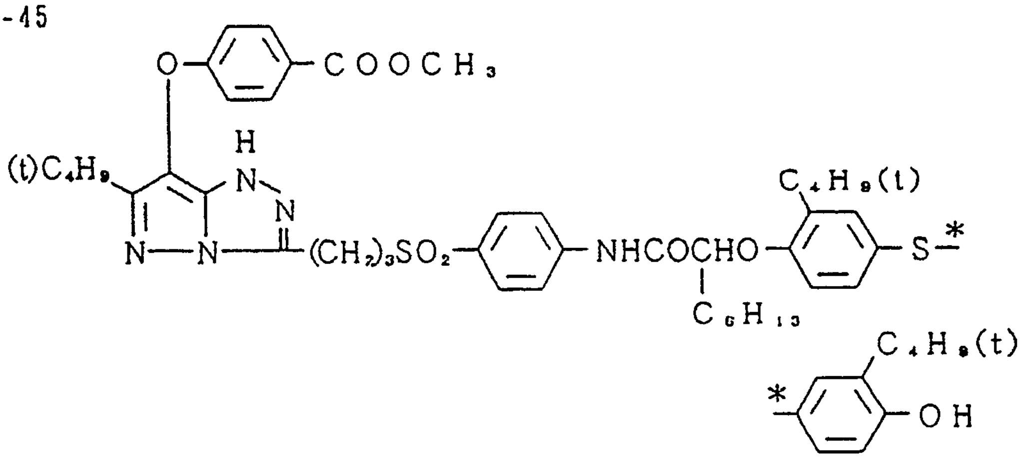

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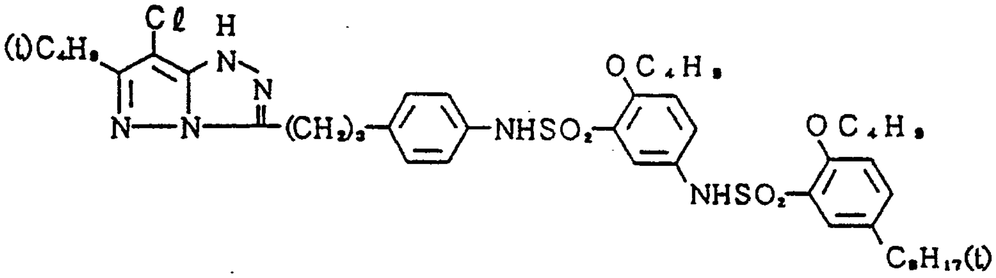

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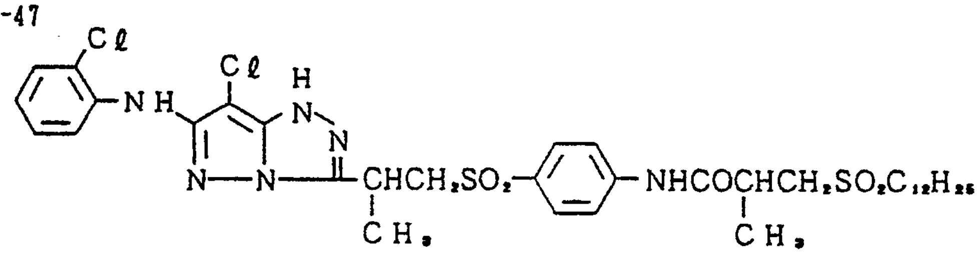

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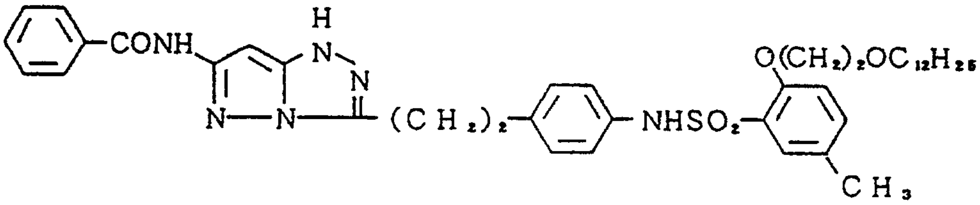

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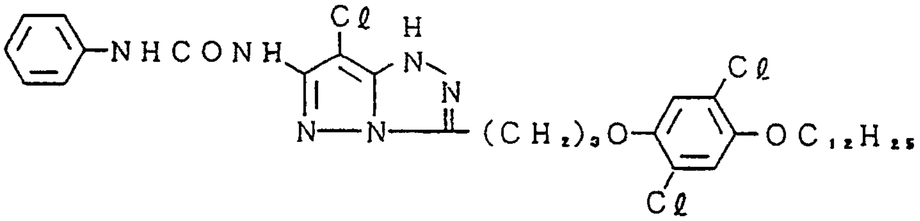

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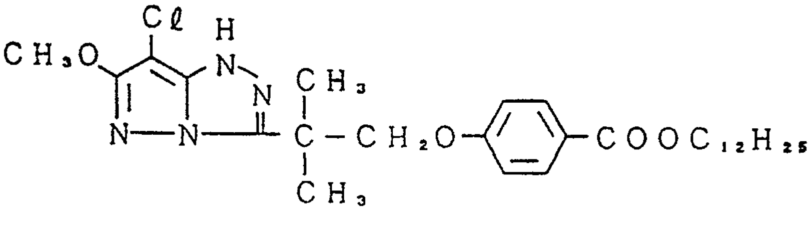

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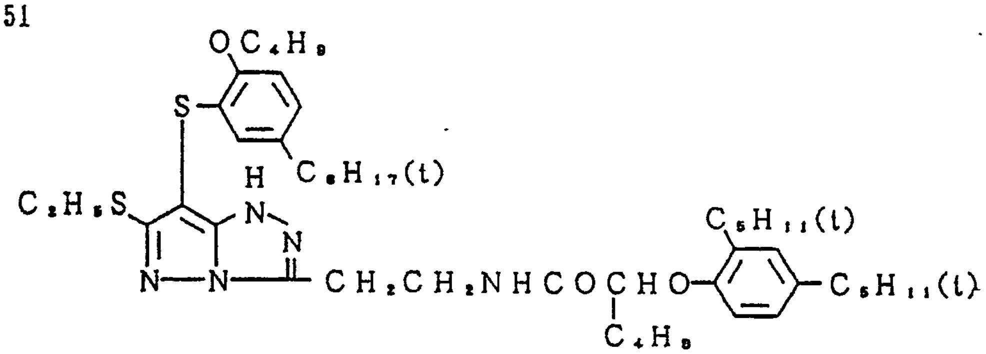

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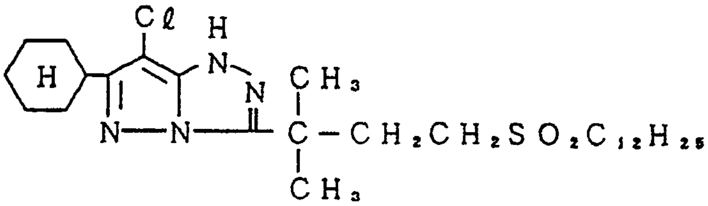

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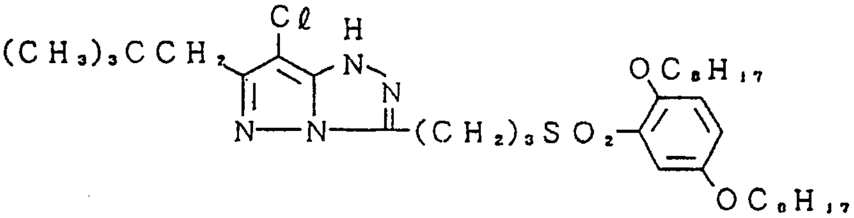

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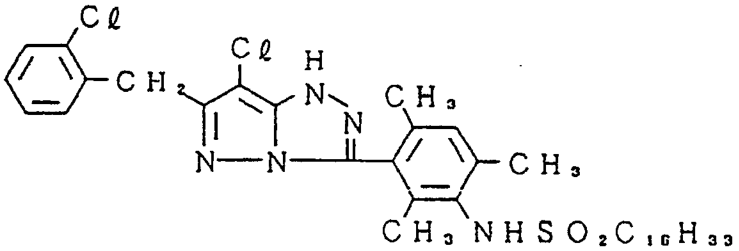

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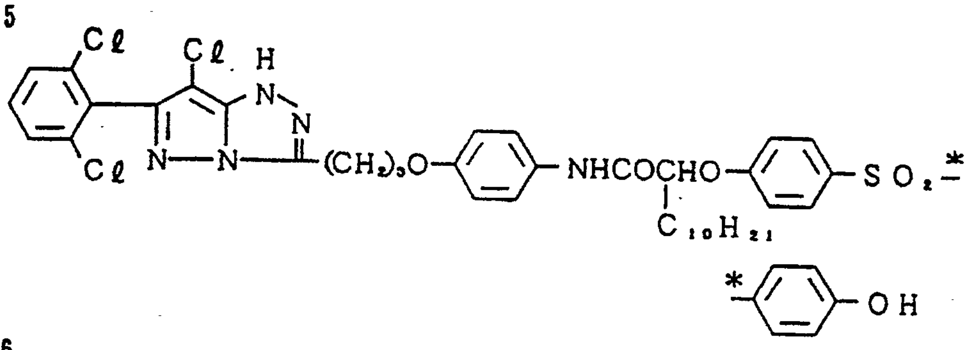

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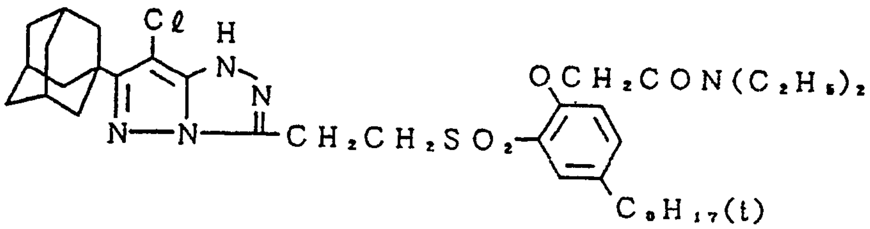

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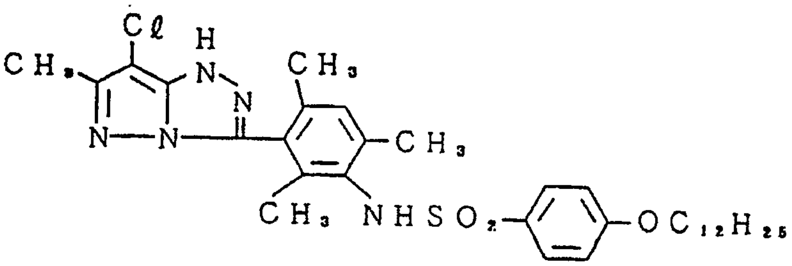

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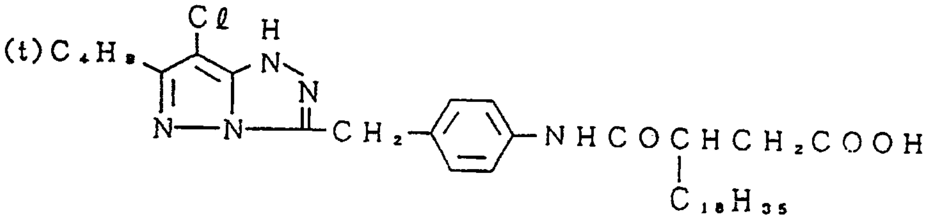

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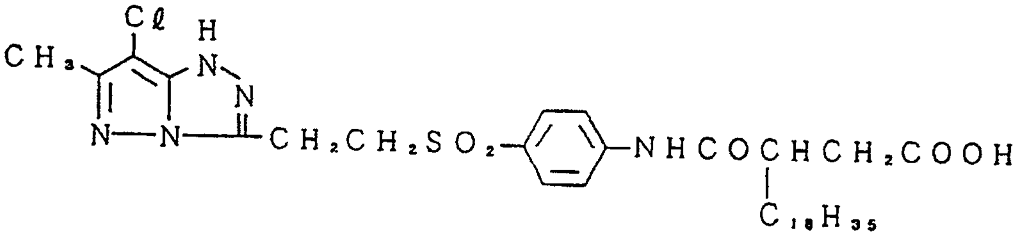

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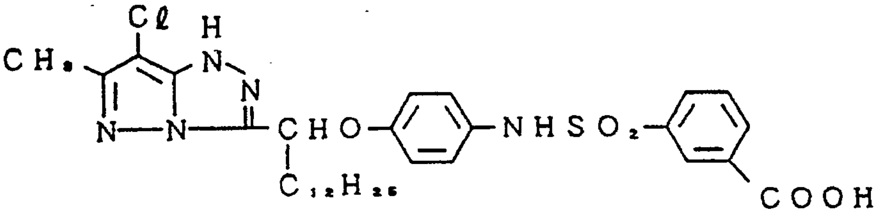

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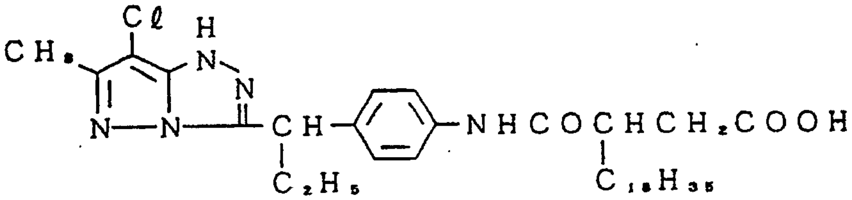

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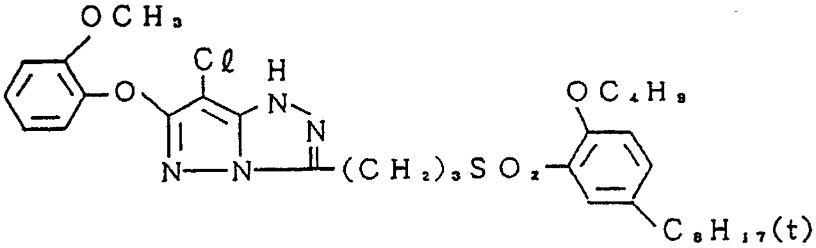

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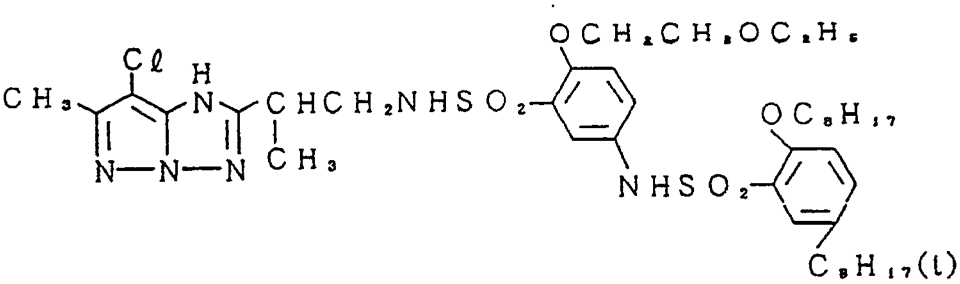

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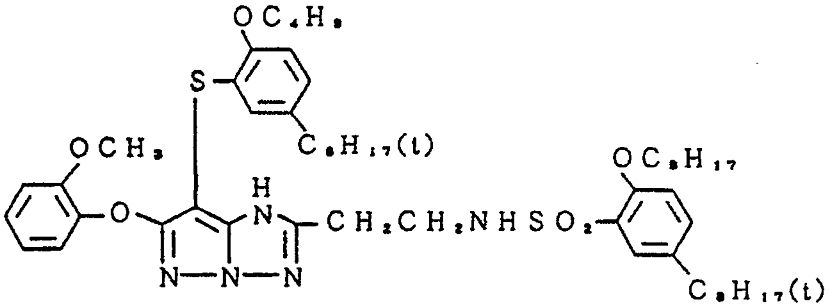
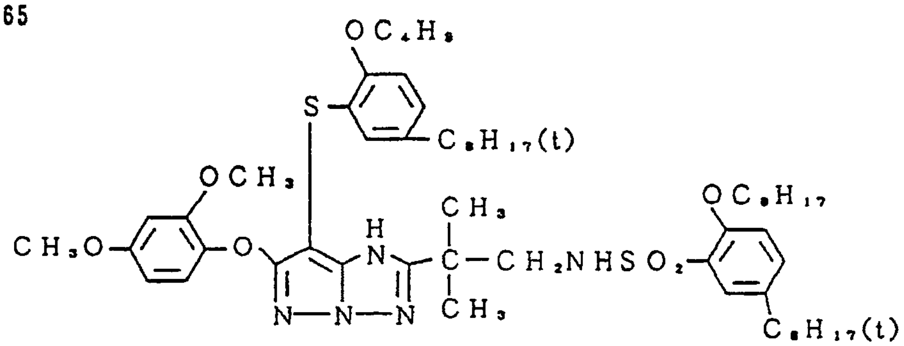
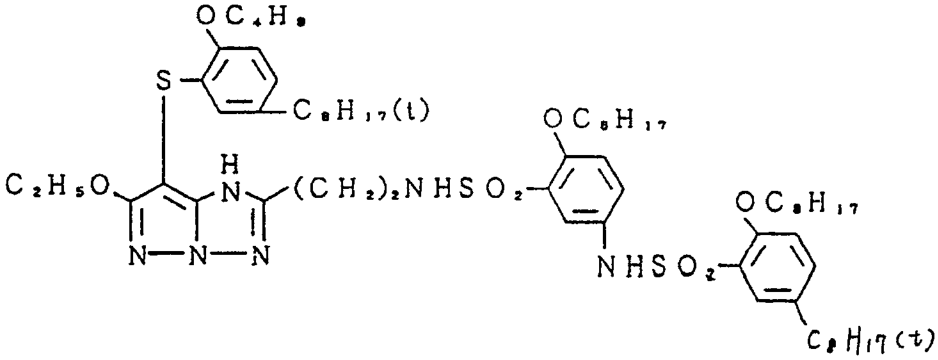

OC4H9
S
C8H17(t)
OCH3
O
H
N
CH2CH2NHSO2
OC8H17
C8H17(t)
N
N
N

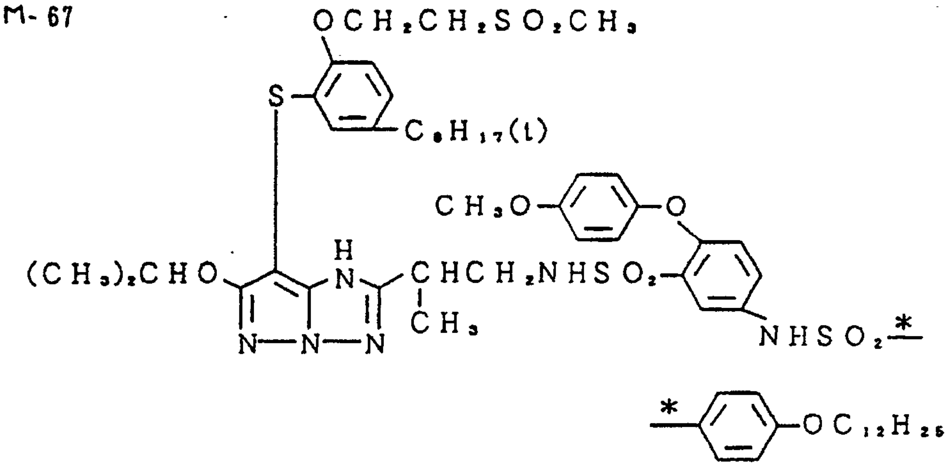
M-65


OC4H9
S
C8H17(t)
OCH3
CH3O
O
H
N
CH3
C
CH2NHSO2
CH3
OC8H17
C8H17(t)
N
N
N

M-66


OC4H9
S
C8H17(t)
C2H5O
H
N
(CH2)2NHSO2
OC8H17
NHSO2
OC8H17
C8H17(t)
N
N
N

M- 67



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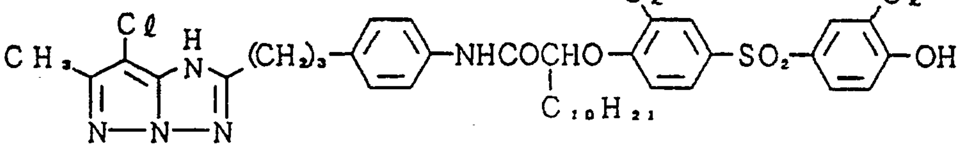
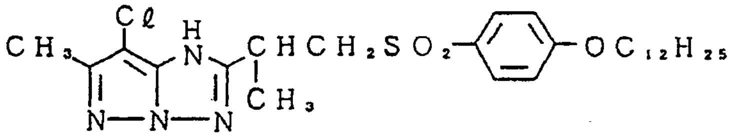
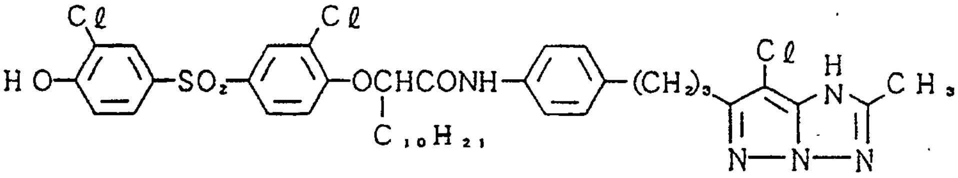


M- 69



M -70



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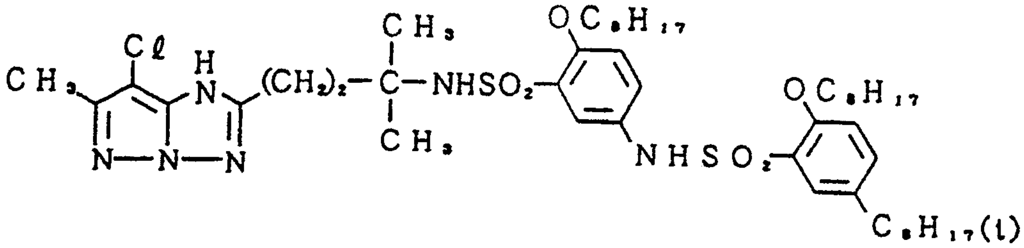

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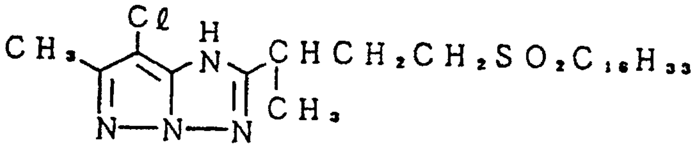

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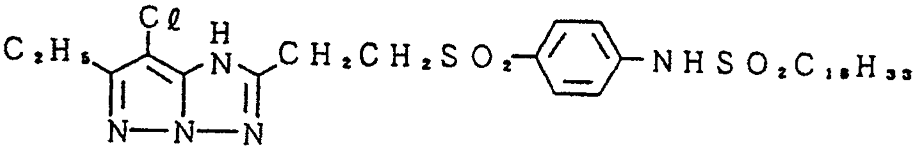

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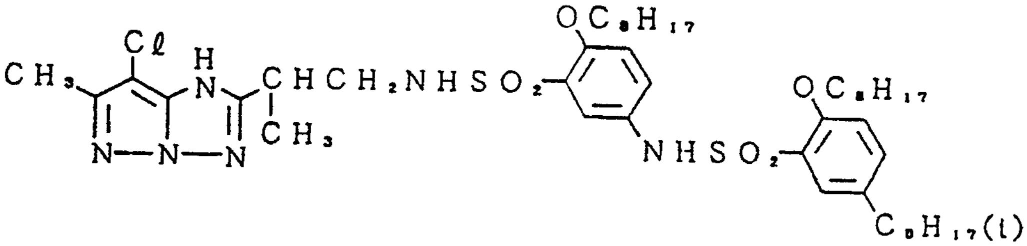

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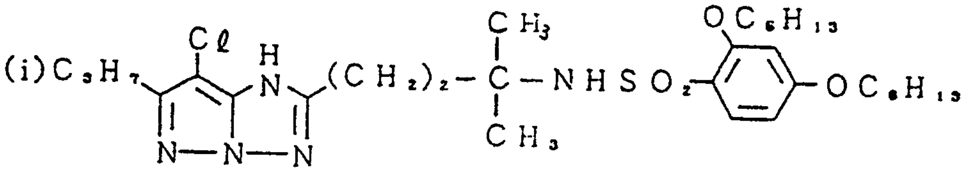

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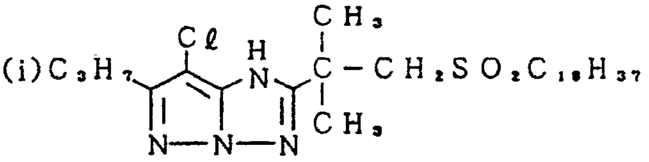

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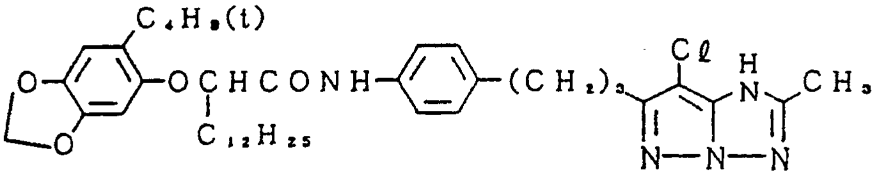

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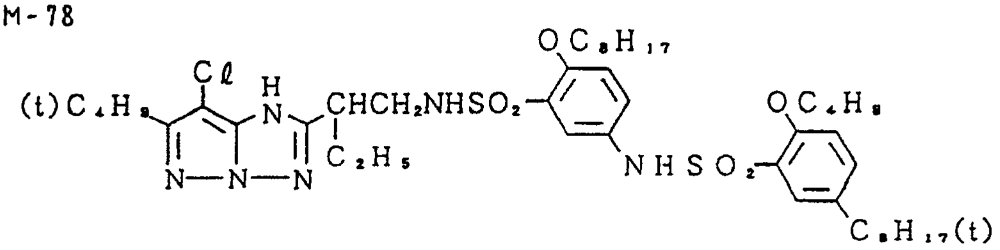

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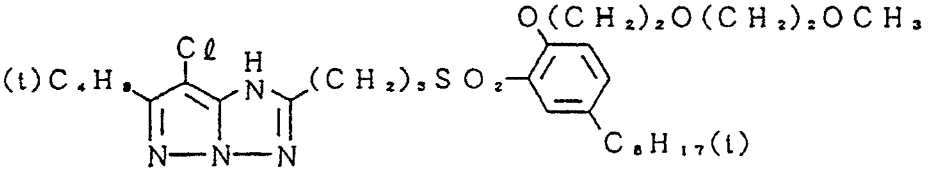

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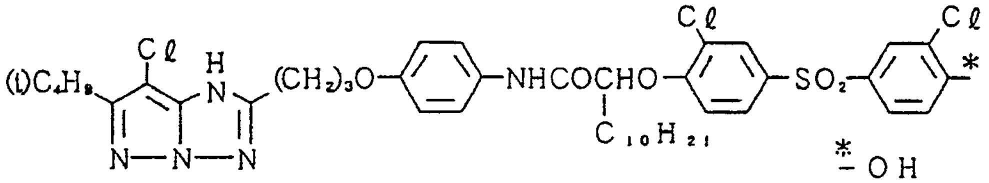
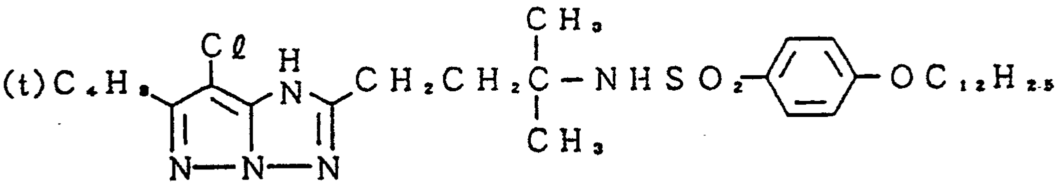


M-81



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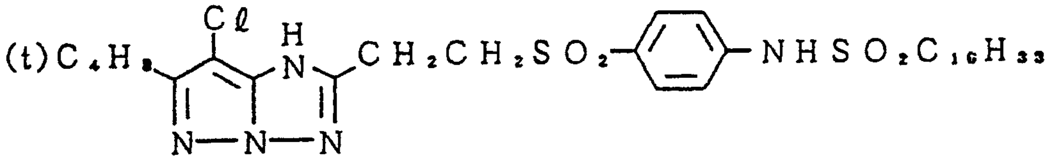

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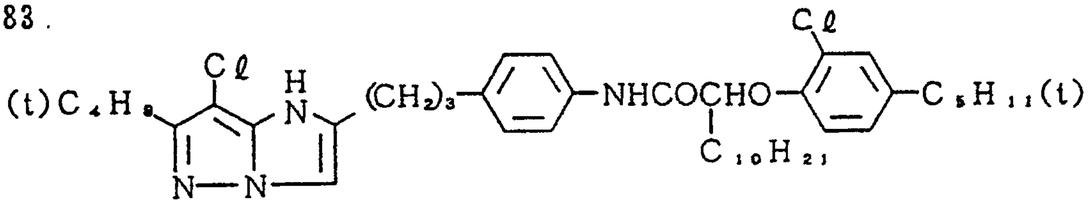

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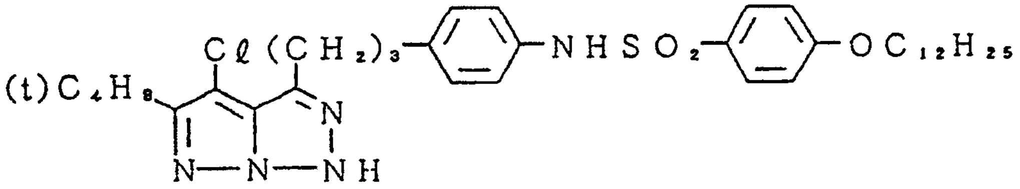
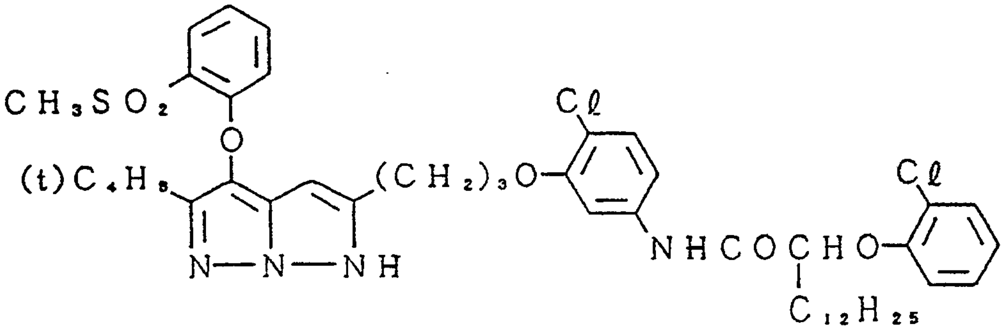
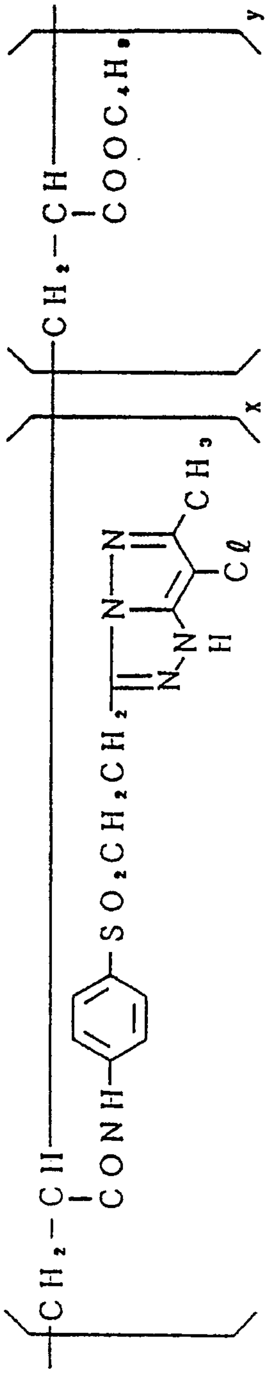


M-85

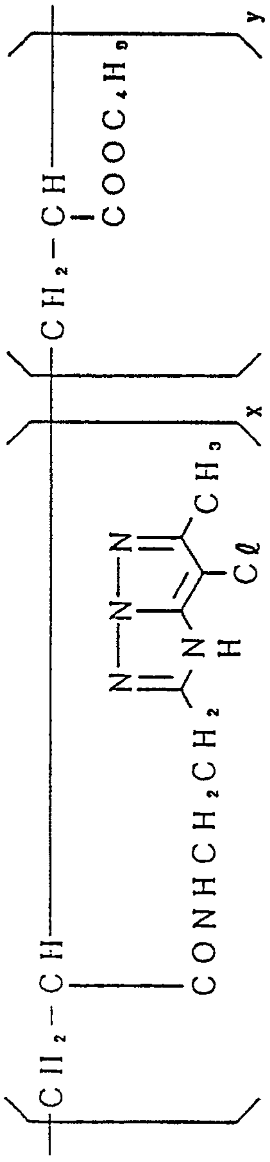


M-87



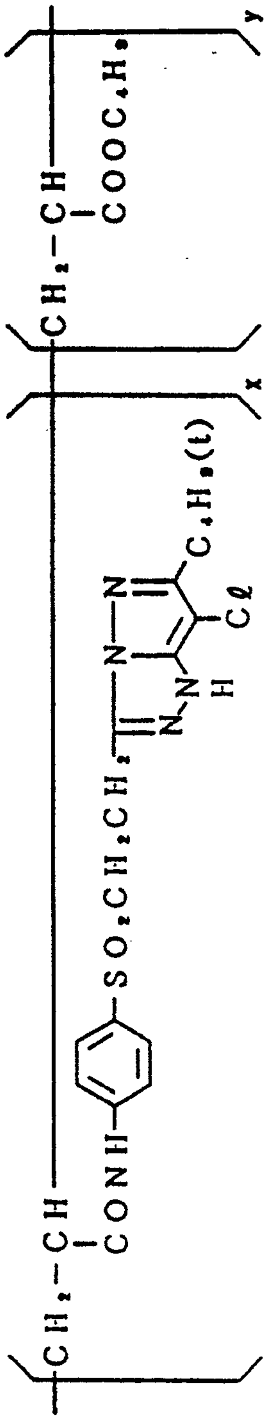
x : y = 50 : 50

M-88



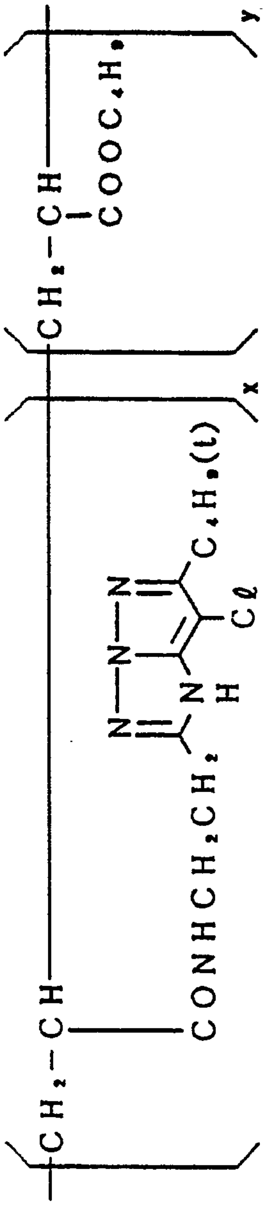
x : y = 50 : 50

M-89



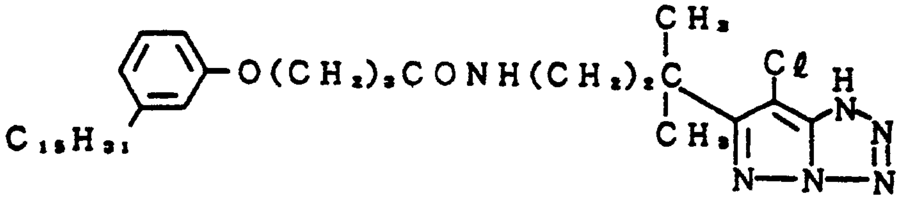
x : y = 50 : 50

M-90



x : y = 50 : 50

M-86



As a specific example of the compound represented by the formula (M-I), in addition to the representative specific examples shown above, there may be mentioned compounds Nos. 1 to 4, Nos. 8 to 17, Nos. 14 to 24, Nos. 26 to 43, Nos. 45 to 59, Nos. 61 to 104, Nos. 106 to 121, Nos. 123 to 162 and Nos. 164 to 223 among the compounds described on p. 66 to p. 122 of Japanese Unexamined Patent Publication No. 166339/1987.

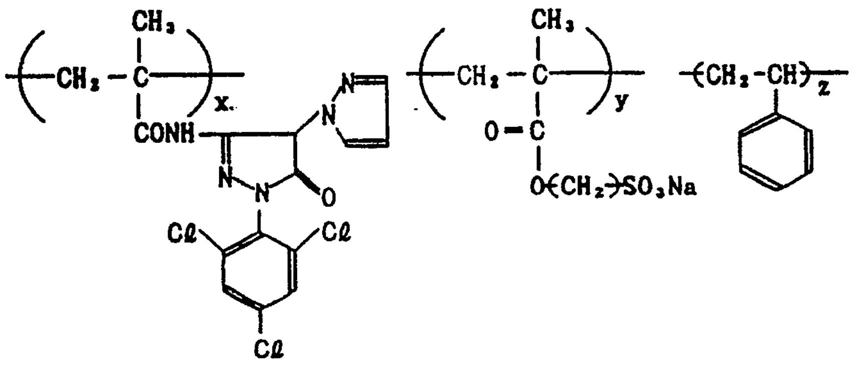
The above couplers can be synthesized by referring to Journal of the Chemical Society, Perkin I (1977), pp. 2047 to 2052, U.S. Patent No. 3,725,067, and Japanese Unexamined Patent Publications No. 99437/1984, No. 42045/1984, No. 162548/1984, No. 171956/1984, No. 33552/1985, No. 43659/1985, No. 172982/1985 and No. 43659/1985.

The magenta coupler represented by the formula (M-I) is used generally in an amount of 1 x 10^{-3} mole to 1 mole, preferably in the range of 1 x 10^{-2} mole to 8 x 10^{-8} mole per mole of silver halide.

Further, the coupler represented by the formula (M-I) can be used in combination with other kinds of magenta dye-forming couplers.

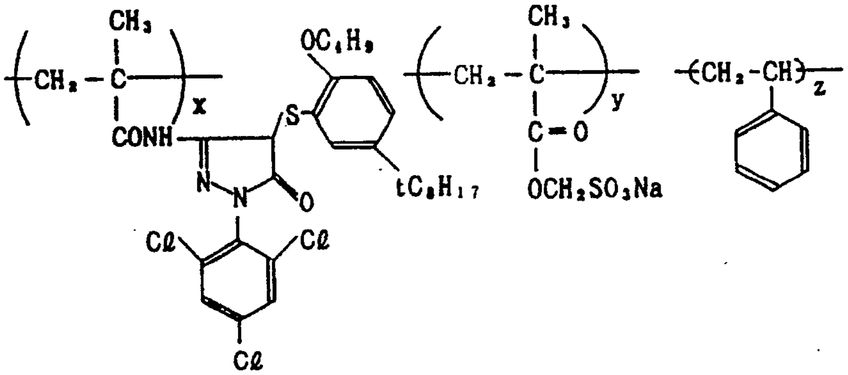
In the present invention, it is also a preferred embodiment to use a polymer coupler. As the polymer coupler, P-2, P-5, P-13, P-14, P-17, P-22 and P-23 disclosed in Japanese Unexamined Patent Publication No. 239748/1985 are preferably used, and further, the following polymer couplers are useful for exhibiting the effect of the present invention.

(PM-1)



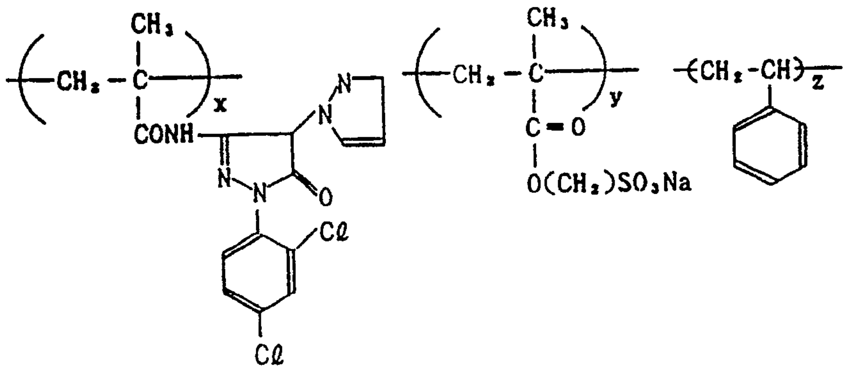
x = 85 % by weight y = 5 % by weight z = 10 % by weight

(PM-2)



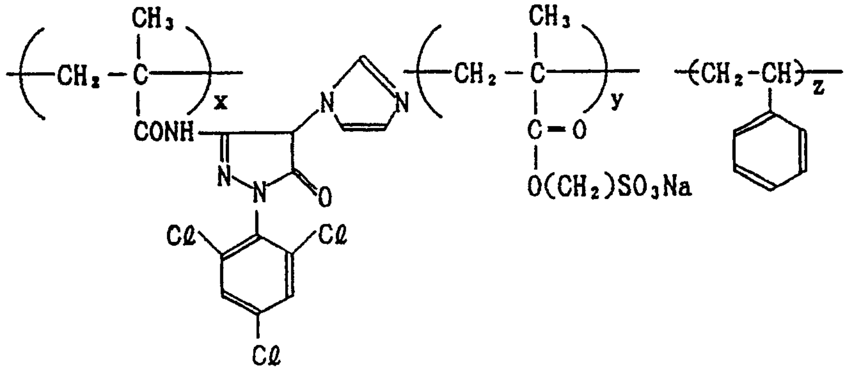
x-85 % by weight y = 5 % by weight z = 10 % by weight

(PM-3)



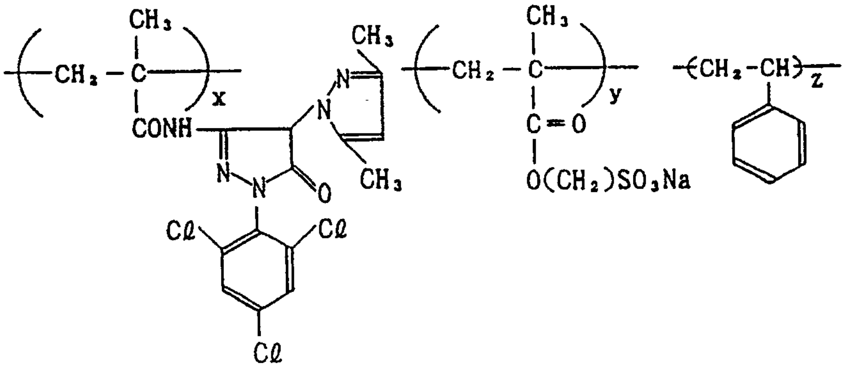
x = 85 % by weight y = 5 % by weight z = 10 % by weight

(PM-4)



x = 85 % by weight y = 5 % by weight z = 10 % by weight

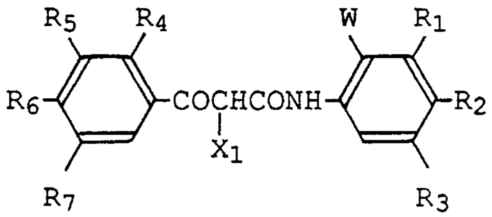
(PM-5)



x = 85 % by weight y = 5 % by weight z = 10 % by weight

When the light-sensitive color photographic material is a light-sensitive material for negative images, a preferred yellow coupler is a benzoylacetanilide type yellow coupler.

The benzoylacetalinide type yellow coupler may include any benzoylacetanilide derivative, but preferred is a compound represented by the following formula (YB-I).

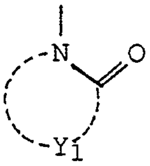

(YB-I)

wherein R_1 to R_7 and X each represent a hydrogen atom or a substituent group; and R_1, R_2, and R_3 may be preferably either the same or different, and each represent a hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alkoxy group, an acylamino group, a carbamoyl group, an alkoxycarbonyl group, a sulfonamide group or a sulfamoyl group.

R_4, R_5, R_6 and R_7 may be the same or different, and preferably, each represent a hydrogen atom, an alkyl group, an alkoxy group, an aryloxy group, an acylamino group or a sulfonamide group.

W represents preferably a halogen atom, an alkyl group, an alkoxy group, an aryloxy group or a dialkylamino group.

X_1 represents a hydrogen atom or an eliminatable group. As the eliminatable group, there may be mentioned, for example, a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, an alkylthio group, an arylthio group, a heterocyclic thio group and a saturated or unsaturated 5-membered or 6-membered nitrogen-containing heterocyclic group, and particularly preferred groups are represented by the formulae (YB-II) and (YB-III).

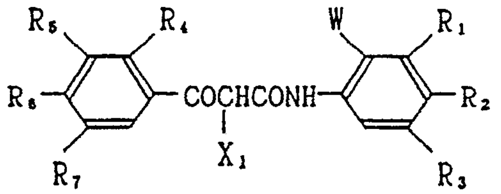

(YB-II)

Y_1 represents a group of non-metallic atoms necessary for forming a 5- or 6-membered ring, and the group of non-metallic atoms may include those having a substituent group.

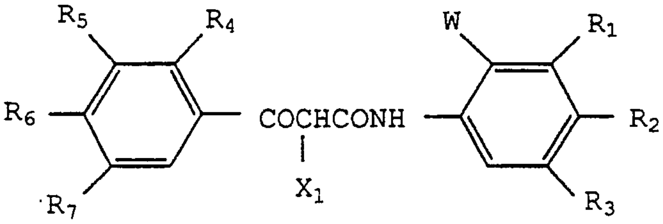
-O-Ar (YB-III)

Ar represents an aryl group, and said aryl group may include those having a substituent group.

In the following, specific examples of the benzoylacetanilide type yellow coupler are shown, but the present invention is not limited to these.



Exemplary compound No.	R1	R2	R3	R4	R5	R6	R7	W	X
YB-1	H	H	(7)	H	H	(4)	H	(1)	(16)
YB-2	H	H	(7)	H	H	(4)	H	(1)	(17)
YB-3	H	H	(8)	H	H	H	H	(1)	(18)
YB-4	H	H	(8)	H	H	H	H	(4)	(19)
YB-5	H	H	(6)	(2)	H	H	H	(4)	(20)
YB-6	H	H	(9)	H	H	(4)	H	(1)	(21)
YB-7	H	H	(11)	H	(10)	(4)	H	(4)	(22)
YB-8	H	H	H	H	H	H	(7)	(4)	(23)
YB-9	H	H	(12)	H	H	(4)	H	(1)	(24)
YB-10	H	H	(13)	H	H	H	H	(1)	(25)
YB-11	H	H	(14)	H	H	(4)	H	(1)	(26)
YB-12	H	H	(15)	H	H	(4)	H	(4)	(27)
YB-13	H	H	H	H	H	(4)	H	(4)	H
YB-14	H	H	H	H	H	(5)	H	(1)	(28)
YB-15	H	H	(6)	H	H	(4)	H	(1)	(17)
YB-16	H	H	(6)	H	H	(4)	H	(1)	(29)
YB-17	H	H	(7)	H	H	(4)	H	(1)	(29)
YB-18	H	H	H	H	H	H	(7)	(4)	H
YB-19	H	H	(30)	(31)	H	H	H	(1)	H
YB-20	H	H	(11)	H	H	(32)	H	(4)	(33)
YB-21	H	H	(34)	H	H	(4)	H	(1)	(35)
YB-22	H	(4)	(4)	H	H	(32)	H	(1)	(36)



Exemplary compound No.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	W	X_1
YB-23	-H	-H	(37)	-H	-H	(4)	-H	(1)	(45)
YB-24	-H	-H	(38)	-H	-H	(4)	-H	(1)	(45)
YB-25	-H	-H	(6)	-H	-H	(39)	-H	(1)	(45)
YB-26	-H	-H	(40)	-H	-H	(4)	-H	(1)	(45)
YB-27	-H	-H	(37)	-H	-H	(4)	-H	(1)	(46)
YB-28	-H	-H	(41)	-H	-H	(4)	-H	(1)	(47)
YB-29	-H	-H	(6)	-H	-H	(4)	-H	(1)	(48)
YB-30	-H	-H	(42)	-H	-H	(4)	-H	(1)	(49)
YB-31	-H	-H	(37)	-H	-H	(4)	-H	(1)	(50)
YB-32	-H	-H	(37)	-H	-H	(4)	-H	(1)	(51)
YB-33	-H	-H	(6)	-H	-H	(4)	-H	(1)	(52)
YB-34	(7)	-H	(43)	(1)	-H	-H	(1)	-H	(53)
YB-35	(44)	-H	(6)	-H	-H	(4)	-H	(1)	(54)
YB-36	-H	-H	(14)	-H	-H	(4)	-H	(1)	(55)
YB-37	-H	-H	(57)	-H	-H	(4)	-H	(1)	(56)
YB-38	-H	-H	(6)	-H	-H	(4)	-H	(1)	(58)

(1)

$-\mathrm{C\ell}$

(2)

$-\mathrm{CH_3}$

(3)

$-\mathrm{C_{18}H_{37}}$

(4)

$-\mathrm{OCH_3}$

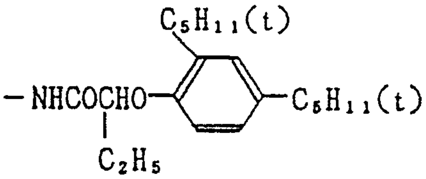
(5)

$-\mathrm{NHCOC_{17}H_{35}}$

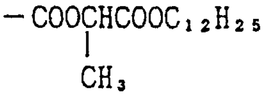
(6)

$-\mathrm{COOC_{12}H_{25}}$

(7)

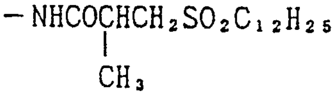


(8)



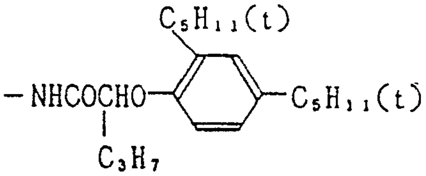
$-\mathrm{COO}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{HCOOC_{12}H_{25}}$

(9)



$-\mathrm{NHCO}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2SO_2C_{12}H_{25}}$

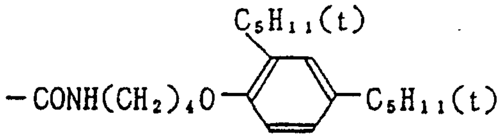
(10)



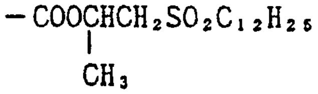
(11)

$-\mathrm{SO_2N(CH_3)_2}$

(12)

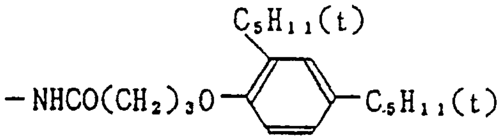


(13)



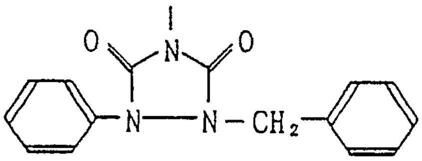
$-\mathrm{COO\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2SO_2C_{12}H_{25}}$

(14)



(15)

(16)



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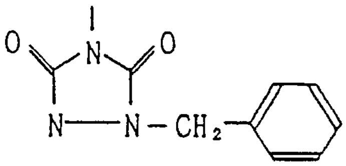

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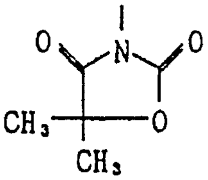

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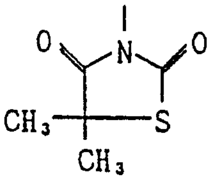

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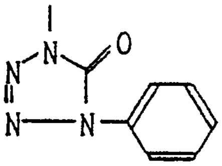
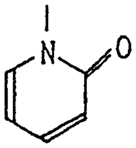


(21)



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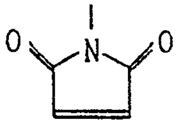

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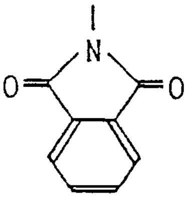

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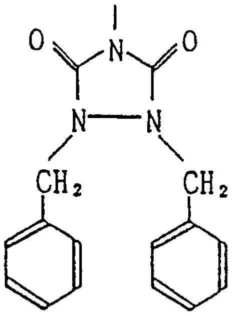

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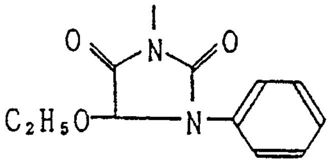

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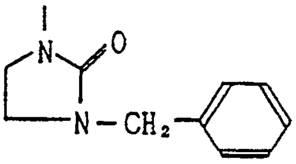

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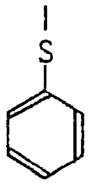

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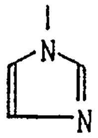

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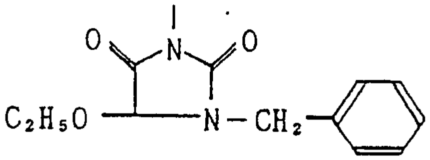
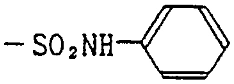


(30)



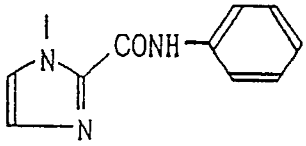
(31)

$-OC_{18}H_{37}$

(32)

$-OC_{16}H_{33}$

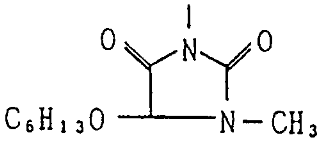
(33)



(34)

$-COOC_8H_{17}$

(35)



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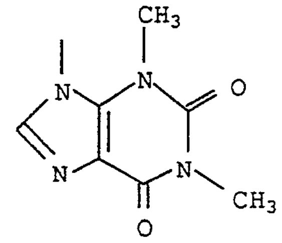
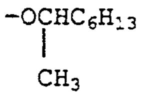


(37) $-NHSO_2C_{16}H_{33}$

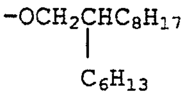
(38) $-OSO_2C_{16}H_{33}$

(39)



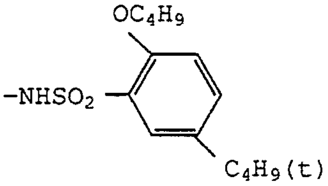
$-O\underset{\underset{CH_3}{|}}{C}HC_6H_{13}$

(40)



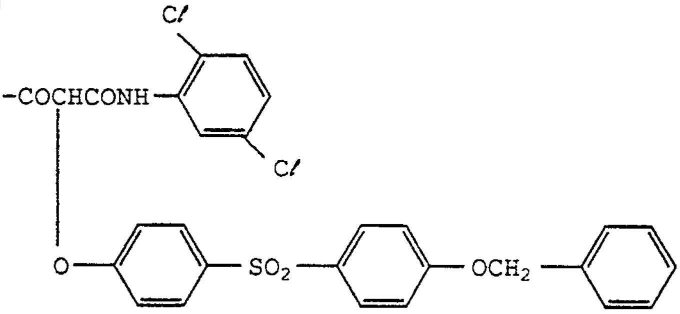
$-OCH_2\underset{\underset{C_6H_{13}}{|}}{C}HC_8H_{17}$

(41)



(42) $-SO_2NHC_{16}H_{33}$

(43)



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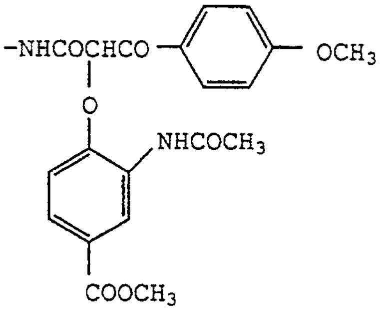

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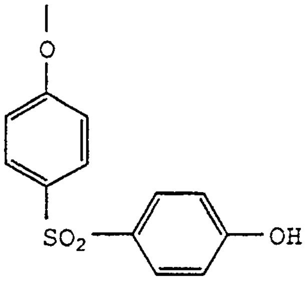

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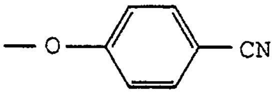
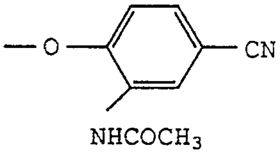


(47)



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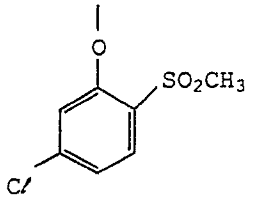

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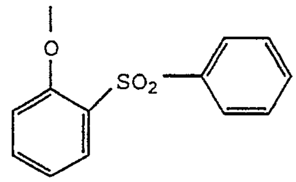

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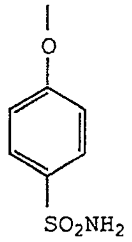

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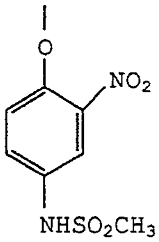
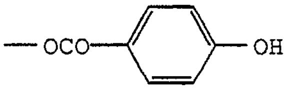


(52)



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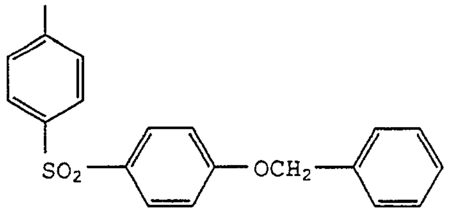

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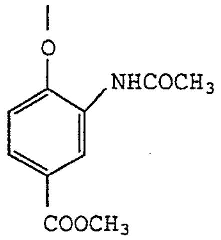

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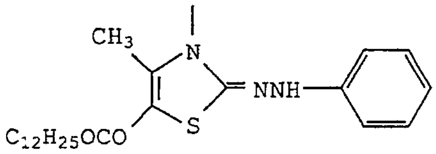

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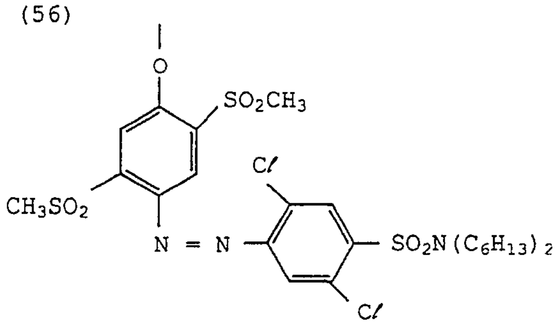
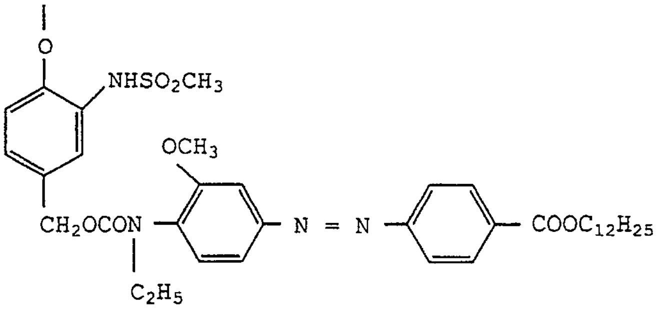


(57)

$-COOC_2H_5$

(58)



These benzoylacetanilide type yellow couplers according to the present invention may include those disclosed in U.S. Patents No. 2,875,057, No. 3,725,072 and No. 3,891,445, Japanese Patent Publication No. 10783/1976, and Japanese Unexamined Patent Publications No. 73147/1973, No. 6341/1975, No. 102636/1976, No. 115219/1977, No. 21448/1979, No. 95237/1981, No. 159163/1984, No. 174838/1984, No. 206835/1984, No. 187560/1989, No. 207748/1989, No. 207749/1989, No. 214848/1989, No. 227152/1989, No. 231050/1989, No. 295256/1989, No. 309057/1989, No. 341240/1989, No. 316744/1989 and No.

316745/1989, and they can be synthesized according to the methods disclosed in the publications.

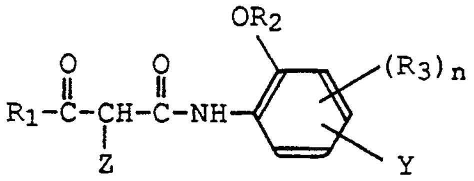
Two or more of the benzoylacetanilide type yellow couplers according to the present invention may be used, and yellow couplers other than these couplers may be used in combination.

For adding the yellow coupler to a light-sensitive material, depending on physical properties (e.g. solubility) of said yellow coupler, various methods such as the oil-in-water type emulsifying dispersion method in which a water-insoluble high boiling point organic solvent is used, the alkali dispersion method in which a coupler is added.in the form of an alkaline solution, the latex dispersion method and the solid dispersion method in which a coupler is added directly in the form of minute solid can be employed.

The total amount of the yellow coupler to be added is generally 1.0 x 10^{-3} mole to 1.0 mole, preferably in the range of 5.0 x 10^{-3} mole to 8.0 x 10^{-1} mole per mole of silver halide.

The benzoylacetanilide type yellow coupler according the present invention is generally contained in a blue-sensitive silver halide emulsion layer, but, depending on a purpose, it may be also contained in a green-sensitive or red-sensitive silver halide emulsion layer having sensitivity to colors other than blue.

When the light-sensitive color photographic material is a light-sensitive material for positive images, a preferred yellow coupler is represented by the following formula (Y-1).



(Y-1)

wherein R_1 represents an alkyl group or a cycloalkyl group; R_2 represents an alkyl group, a cycloalkyl group, an acyl group or an aryl group; R_3 represents a group with which a benzene ring can be substituted; n represents 0 or 1; Y represents a monovalent ballast group; and Z represents a hydrogen atom, or an atom or a group which can be eliminated at the time of coupling.

In the formula (Y-1), the alkyl group represented by R_1 may be straight or branched, and may include, for example, a methyl group, an ethyl group, an isopropyl group, a t-butyl group and a dodecyl group. These alkyl groups may further include those having a substituent group, and as the substituent group, there may be mentioned, for example, a halogen atom and each group of aryl, alkoxy, aryloxy, alkylsulfonyl, acylamino and hydroxy.

The cycloalkyl group represented by R_1 may include a cyclopropyl group, a cyclohexyl group and an adamantyl group.

R_1 is preferably a branched alkyl group. As the alkyl group and the cycloalkyl group represented by R_2, there may be mentioned the same groups in the case of R_1, and as the aryl group, there may be mentioned, for example, a phenyl group. These alkyl groups, cycloalkyl groups and aryl groups represented by R_2 may include those having a substituent group similarly as in the case of R_1. As the acyl group, there may be mentioned, for example, an acetyl group, a propionyl group, a butyryl group, a hexanoyl group and a benzoyl group.

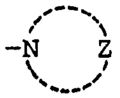
R_2 is preferably an alkyl group and an aryl group, more preferably an alkyl group.

R_3 is not particularly limited as long as it is a group with which a benzene ring can be substituted, and may specifically include a halogen atom (e.g. a chlorine atom), an alkyl group (e.g. an ethyl group, an i-propyl group and a t-butyl group), an alkoxy group (e.g. a methoxy group), an aryloxy group (e.g. a phenyloxy group), an acyloxy group (e.g. a methylcarbonyloxy group and a benzoyloxy group), an acylamino group (e.g. an acetamide group and a phenylcarbonylamino group), a carbamoyl group (e.g. an N-methylcarbamoyl group and an N-phenylcarbamoyl group), an alkylsulfonamide group (e.g. an ethylsulfonylamino group), an arylsulfonamide group (e.g. a phenylsulfonylamino group), a sulfamoyl group (e.g. an N-propylsulfamoyl group and an N-phenylsulfamoyl group) and an imide group (e.g. a succinimide group and a glutarimide group).

In the formula (Y-1), Z represents a group which is eliminated at the time of coupling reaction with an oxidized product of a developing agent, and, for example, represents a group represented by the following formula (Y-2) or (Y-3).

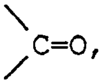
$-OR_{10}$ (Y-2)

In the formula (Y-2), R_{10} represents an aryl group or a heterocyclic group including those having a substituent group.



(Y-3)

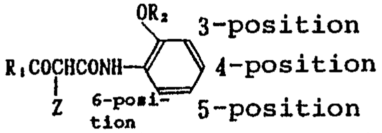
In the formula (Y-3), Z represents a group of non-metallic atoms necessary for forming a 5- or 6-membered ring together with a nitrogen atom. Here, atoms necessary for forming the group of non-metallic atoms may include, for example methylene, methine, substituted methine,

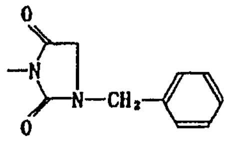
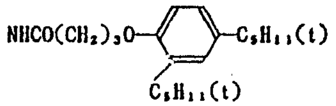
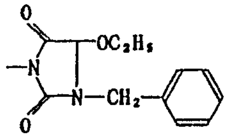
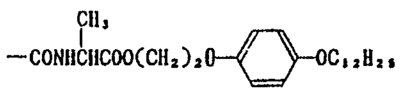
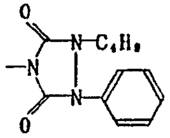
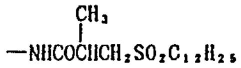
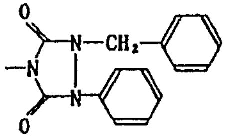
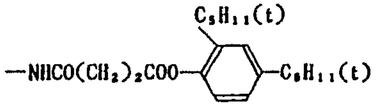
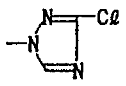
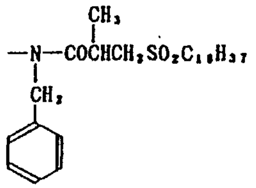


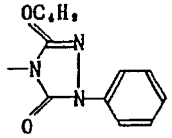
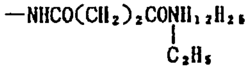
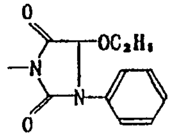
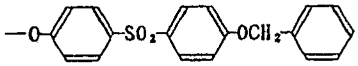
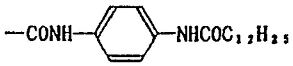
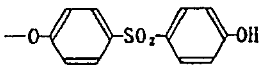
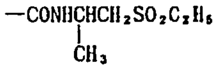
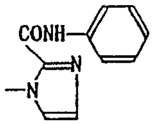
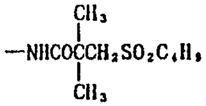
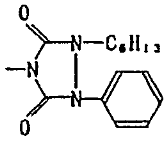
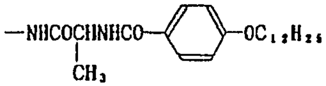
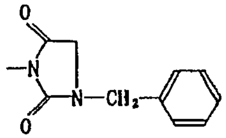
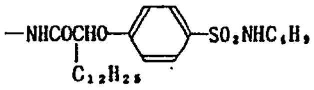
-NH-, -N=, -O-, -S- and $-SO_2-$.

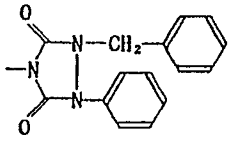
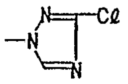
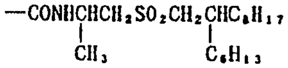
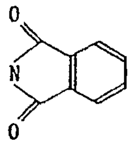
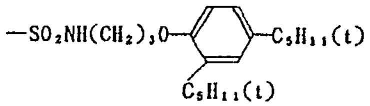
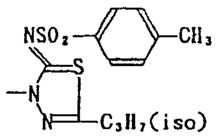
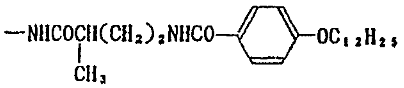
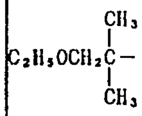
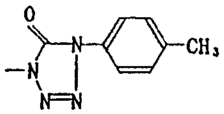
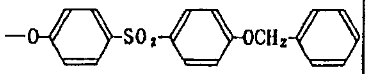
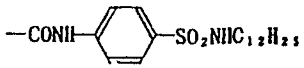
The yellow dye-forming coupler represented by the above formula (Y-1) of the present invention can be used generally in an amount of 1 x 10^{-3} mole to 1 mole, preferably in the range of 1 x 10^{-2} mole to 8 x 10^{-1} mole per mole of silver halide.

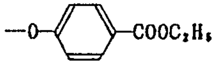
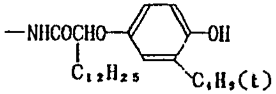
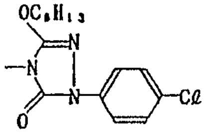
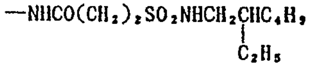
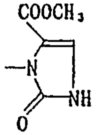
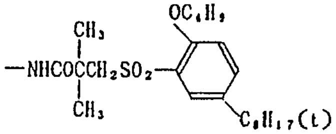
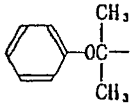
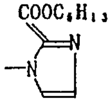
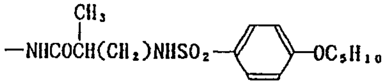
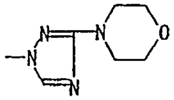
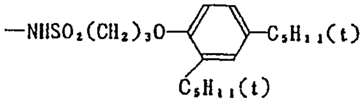
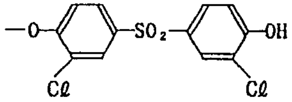
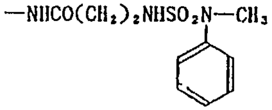
Next, specific examples of the yellow coupler represented by the above formula (Y-1) are shown below.

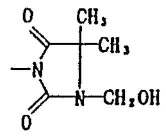
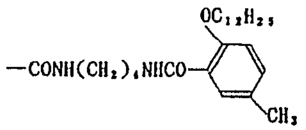
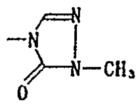
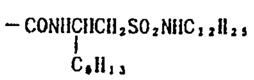
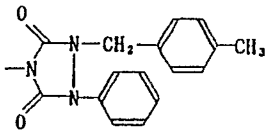
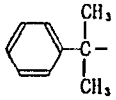
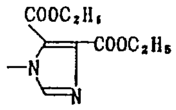
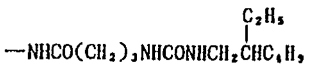
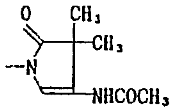
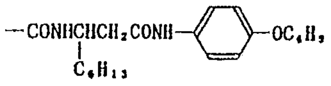
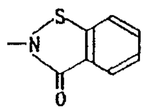


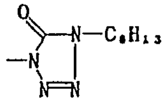
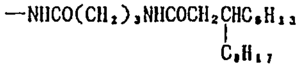
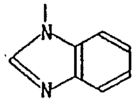
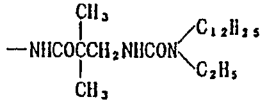
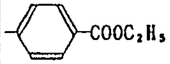
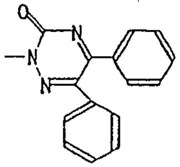
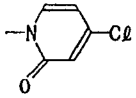
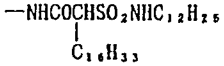
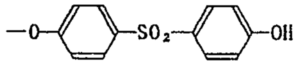
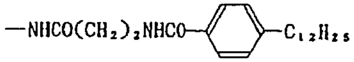
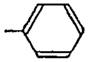
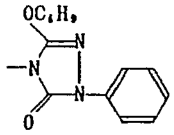
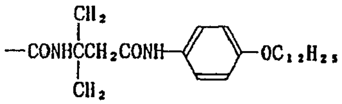
No.	R₁	R₂	Z	3-position	4-position	5-position	6-position
Y-1-1	(t)C_4H_9—	—CH_3		—H	—H		—H
Y-1-2	(t)C_4H_9—	—CH_3		—H	—H		—H
Y-1-3	(t)C_4H_9—	—CH_3		—H	—H	 $-NHCOCH(CH_3)CH_2SO_2C_{12}H_{25}$	—H
Y-1-4	(t)C_4H_9—	—CH_3		—H	—H		—H
Y-1-5	(t)C_4H_9—	—CH_3		—H	—H		—H

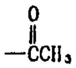
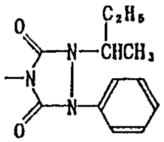
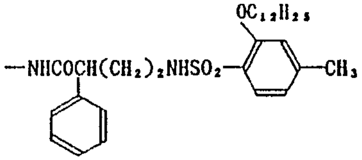
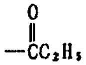
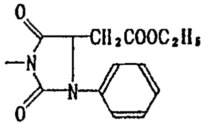
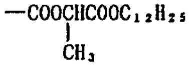
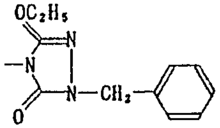
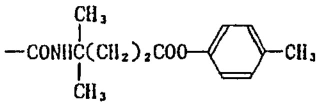
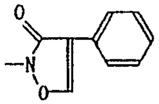
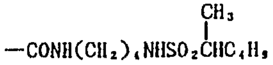
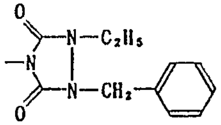
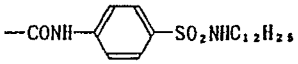
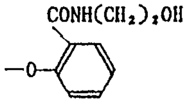
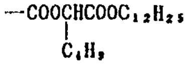
No.	R₁	R₂	Z	3-position	4-position	5-position	6-position
Y-1-6	$(t)C_4H_9-$	$-CH_3$		—H	—H	 $-\mathrm{NHCO(CH_2)_2CO\underset{\substack{\mid\\ C_2H_5}}{N}H_{12}H_{25}}$	—H
Y-1-7	$(t)C_4H_9-$	$-C_3H_7(iso)$		—H	—H		—H
Y-1-8	$(t)C_4H_9-$	$-CH_3$		—H	—H		—H
Y-1-9	$(t)C_4H_9-$	$-C_{12}H_{25}$		—H	—H	 $-\mathrm{CONH\underset{\substack{\mid\\ CH_3}}{C}HCH_2SO_2C_2H_5}$	—H
Y-1-10	$(t)C_4H_9-$	$-C_{18}H_{37}$		—H	—H	 $-\mathrm{NHCO\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ CH_3}}{C}}CH_2SO_2C_4H_9}$	—H
Y-1-11	$(t)C_4H_9-$	$-CH_3$		—H	—H		—H
Y-1-12	$(t)C_4H_9-$	$-C_4H_9$		—H	—H		—H

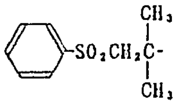
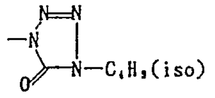
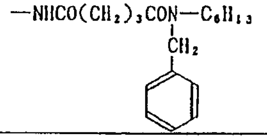
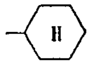
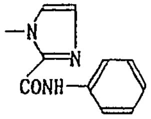
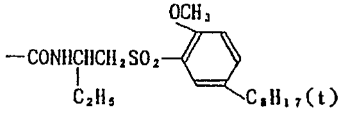
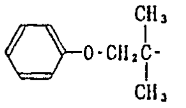
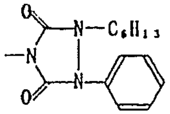
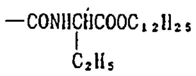
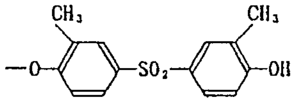
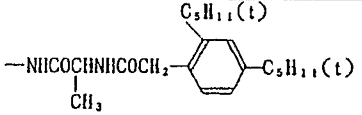
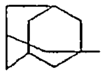
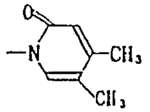
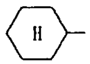
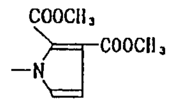
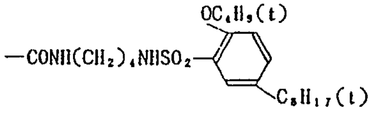
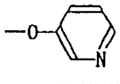
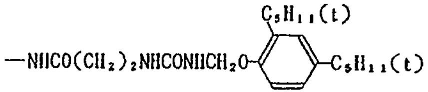
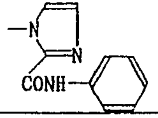
No.	R₁	R₂	Z	3-position	4-position	5-position	6-position
Y-1-13	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$	$-CONH(CH_2)_2NHSO_2C_{12}H_{25}$	$-H$
Y-1-14	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$	 $-CONH\underset{CH_3}{\underset{\vert}{C}}HCH_2SO_2CH_2\underset{C_6H_{13}}{\underset{\vert}{C}}HC_8H_{17}$	$-H$
Y-1-15	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$		$-H$
Y-1-16	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$		$-H$
Y-1-17	 $C_2H_5OCH_2\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-$	$-CH_3$		$-H$	$-H$	$-NHCO(CH_2)_{10}COOC_2H_5$	$-H$
Y-1-18	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$		$-H$

No.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-1-19	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$		$-H$
Y-1-20	$(t)C_4H_9-$	$-C_{12}H_{25}$		$-H$	$-H$	 $-NHCO(CH_2)_2SO_2NHCH_2CHC_4H_9$ (C_2H_5 on CH)	$-H$
Y-1-21	$(t)C_4H_9-$	$-C_2H_5$		$-H$	$-Cl$		$-H$
Y-1-22		$-C_4H_9$		$-H$	$-H$	$-NHSO_2C_{16}H_{33}$	$-H$
Y-1-23	$(t)C_5H_{11}$	$-C_2H_5$	H	$-H$	$-H$		$-H$
Y-1-24	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$		$-H$
Y-1-25	$(t)C_4H_9-$	$-C_{18}H_{37}$		$-H$	$-H$		$-H$

No.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-1-26	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$		$-H$
Y-1-27	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$	 $-CONH\underset{C_6H_{13}}{\underset{\vert}{C}}HCH_2SO_2NHC_{12}H_{25}$	$-H$
Y-1-28	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$	$-COOC_{12}H_{25}$	$-H$
Y-1-29		$-C_{12}H_{25}$		$-H$	$-H$	 $-NHCO(CH_2)_3NHCONHCH_2\overset{C_2H_5}{\overset{\vert}{C}}HC_4H_9$	$-H$
Y-1-30	$(t)C_5H_{11}-$	$-CH_3$		$-H$	$-H$		$-H$
Y-1-31	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$	$-COOC_{18}H_{35}$	$-H$

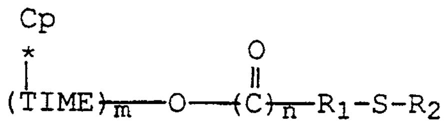
No.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-1-32	$(t)C_4H_9-$	$-CH_3$		$-H$	$-H$	 $-NHCO(CH_2)_3NHCOCH_2\underset{\mid}{C}HC_6H_{13}$ C_8H_{17}	$-H$
Y-1-33	$(t)C_4H_9-$	$-CH_3$		$-H$	$-Cl$	 $-NHCOC(CH_3)_2CH_2NHCON(C_{12}H_{25})(C_2H_5)$	$-H$
Y-1-34	$(t)C_4H_9-$			$-H$	$-H$		$-H$
Y-1-35	$(t)C_4H_9-$	$-C_4H_9$		$-H$	 $-NHCO\underset{\mid}{C}HSO_2NHC_{12}H_{25}$ $C_{16}H_{33}$	$-Cl$	$-H$
Y-1-36	$(t)C_4H_9-$	$-CH_3$		$-H$	$-Cl$		$-H$
Y-1-37	$(t)C_4H_9-$			$-H$	$-H$		$-H$

No.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-1-38	$(t)C_5H_{11}$—	 $-\overset{O}{\overset{\parallel}{C}}CH_3$		—H	$-OCH_3$		—H
Y-1-39	$(t)C_4H_9$—	 $-\overset{O}{\overset{\parallel}{C}}C_2H_5$		—H	—H	 $-COO\underset{CH_3}{\underset{\vert}{C}}HCOOC_{12}H_{25}$	—H
Y-1-40	$(t)C_4H_9$—	$-CH_3$		—H	—H		—H
Y-1-41	$(t)C_4H_9$—	$-CH_3$		—H	 $-CONH(CH_2)_4NHSO_2\overset{CH_3}{\overset{\vert}{C}}HC_4H_9$	$-OCH_3$	—H
Y-1-42	$(t)C_4H_9$—	$-CH_3$		—H	—H		—H
Y-1-43	$(t)C_4H_9$—	$-CH_3$		—H	—H	 $-COO\underset{C_4H_9}{\underset{\vert}{C}}HCOOC_{12}H_{25}$	—H

No.	R₁	R₂	Z	3-position	4-position	5-position	6-position
Y-1-44		$-C_2H_5$		—H	—H		—H
Y-1-45	$(t)C_4H_9-$			—H	—H		—H
Y-1-46		$-CH_3$		—H	—H	 $-CONHCH(C_2H_5)COOC_{12}H_{25}$	—H
Y-1-47	$(iso)C_3H_7-$	$-C_4H_9$		—H	—H		—H
Y-1-48		$-CH_3$		—H	—H	$-NHCO(CH_2)_{10}COOC_2H_5$	—H
Y-1-49		$-CH_3$		—H	—H		—H
Y-1-50	$(t)C_4H_9-$	$-CH_3$		—H	—H		—H
Y-1-51	$(t)C_4H_9-$	$-C_{16}H_{33}$		—H	—H	$-SO_2NHCOC_2H_5$	—H

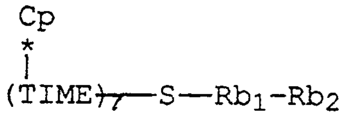
In the light-sensitive silver halide color photographic material to be used in the present invention, particularly the light-sensitive material for negative images, when a compound which releases a bleaching accelerator by reaction with an oxidized product of a color developing agent (hereinafter called "a BAR compound") is contained in at least one silver halide emulsion layer, the effect of the present invention can be exhibited more favorably.

As the BAR compound preferably used, there may be mentioned compounds represented by the following formulae (BAR-A) and (BAR-B).



$$\underset{\text{(TIME)}_m}{\overset{\overset{Cp}{*}}{|}}\text{-O-}(\overset{O}{\overset{\|}{C}})_n\text{-}R_1\text{-S-}R_2$$

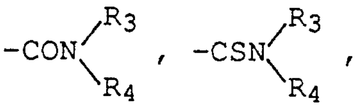
(BAR-A)

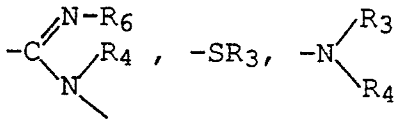


$$\underset{\text{(TIME)}_\ell}{\overset{\overset{Cp}{*}}{|}}\text{-S-}Rb_1\text{-}Rb_2$$

(BAR-B)

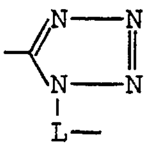
wherein Cp represents a coupler residue which can undergo coupling reaction with an oxidized product of a color developing agent; * represents a coupling position of the coupler; TIME represents a timing group, m and ℓ each represent 0 or 1; R_1 represents a bonding group (preferably an alkylene group having 1 to 8 carbon atoms); and R_2 represents a hydrogen atom, a cyano group, $-COR_3$, $-CSR_3$,





or a hetero ring (where R_3 represents an alkyl group and an aryl group; and R_4, R_5 and R_6 each represent a hydrogen atom, an alkyl group and an aryl group).

Rb_1 represents a divalent aliphatic group having 1 to 8 carbon atoms or



(where L represents a divalent aliphatic group having 1 to 8 carbon atoms or a phenylene group), and Rb_2 represents a water-soluble group or a precursor thereof.

In the above formula, the coupler residue represented by Cp may generally include a residue which forms an yellow, magenta or cyan dye and a residue which forms a substantially colorless product.

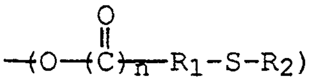
In the coupler residue represented by Cp, as a representative yellow coupler residue, there may be mentioned, for example, those disclosed in U.S. Patents No. 2,298,443, No. 2,407,210, No. 2,875,057, No. 3,048,194, No. 3,265,506 and No. 3,447,928, and Farbkupp-lereine Literaturuversiecht Agfa Mitteilung (Band II), pp. 112 to 126 (1961). Among these, acylacetanilides, for example, benzoylacetanilides and pivaloylacetanilides are preferred.

As a representative magenta coupler residue, there may be mentioned, for example, those disclosed in U.S. Patents No. 2,369,489, No. 2,343,703, No. 2,311,182, No. 2,600,788, No. 2,908,573, No. 3,062,653, No. 3,152,896, No. 3,519,429, No. 3,725,067 and No. 4,540,654, Japanese Unexamined Patent Publication No. 162548/1984, and the above Agfa Mitteilung (Band II), pp. 126 to 156 (1961). Among these, pyrazolones or pyrazoloazoles (e.g. pyrazoloimidazole and pyrazolotriazole) are preferred.

As a representative cyan coupler residue, there may be mentioned, for example, those disclosed in U.S. Patents No. 2,367,531, No. 2,423,730, No. 2,472,293, No. 2,772,162, No. 2,395,826, No. 3,002,836, No. 3,034,892, No. 3,041,236 and No. 4,666,999, and the above Agfa Mitteilung (Band II), pp 156 to 175 (1961). Among these, phenols or naphthols are preferred.

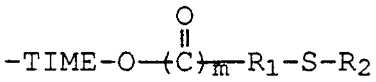
As a representative coupler residue which forms a substantially colorless product, there may be mentioned, for example, those disclosed in U.K. Patent No. 861,138, U.S. Patents No. 3,632,345, No. 3,928,041, No. 3,958,993 and No. 3,961,959. Among these, cyclic carbonyl compounds are preferred.

The timing group represented by TIME is a group which enables releasing of a bleaching accelerator group,



$$-(O-(\overset{\overset{O}{\|}}{C})_n-R_1-S-R_2)$$

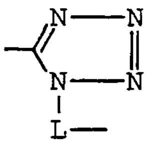
or $(S\text{-}Rb_1\text{-}Rb_2)$ from Cp under time control, and in this group, a group which can control a speed of reaction between Cp and an oxidized product of a color developing agent, a diffusion speed of



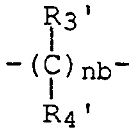
$$-TIME-O-(\overset{\overset{O}{\|}}{C})_m-R_1-S-R_2$$

or -TIME-S-Rb_1-Rb_2 released from Cp, and a releasing speed of said bleaching accelerator group may be contained. As a representative timing group, there may be mentioned a group which releases a bleaching accelerator group by the intermolecular nucleophilic substitution reaction disclosed in U.S. Patent No. 4,248,962 and Japanese Unexamined Patent Publication No. 56837/1982, and a group which releases a bleaching accelerator group by the electron transfer reaction along with conjugated chains disclosed in Japanese Unexamined Patent Publications No. 114946/1981 and No. 154234/1982. Additionally, there may be included timing groups disclosed in Japanese Unexamined Patent Publications No. 188035/1982, No. 98728/1983, No. 206834/1984, No. 7429/1985, No. 214358/1985, No. 225844/1975, No. 229030/1985, No. 233649/1985, No. 237446/1985 and No. 237447/1985.

In -S-Rb_1-Rb_2 which is one of the bleaching accelerator groups, Rb_1 represents a divalent aliphatic group having 1 to 8 carbon atoms or



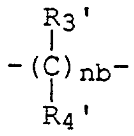
(where L represents a divalent aliphatic group having 1 to 8 carbon atoms or a phenylene group), but preferably, it is represented by the following formula:



$$-(\underset{\underset{R_4'}{|}}{\overset{\overset{R_3'}{|}}{C}})_{nb}-$$

wherein R_3' and R_4' each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms; nb represents 1 to 8; and when nb is two or more, each R_3' and R_4' may be the same or different.

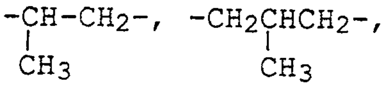
The alkyl group represented by R_3' and R_4' may be straight or branched, and may include, for example, a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group and a tert-butyl group. As a preferred group of R_1 in the formula (BAR-A), there may be mentioned a group having the same meaning as



$$-\underset{R_4'}{\overset{R_3'}{(C)}}{}_{nb}-$$

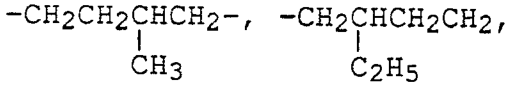
which is described as the preferred group of the above Rb_1.

In the following, preferred examples as Rb_1 are shown. $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,

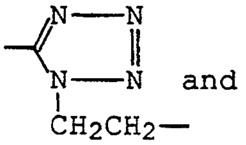


$$-\underset{CH_3}{CH}-CH_2-,\quad -CH_2\underset{CH_3}{CH}CH_2-,$$

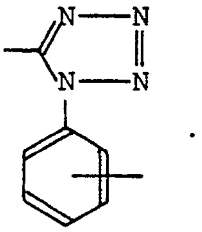
$-CH_2CH_2CH_2CH_2-$,



$$-CH_2CH_2\underset{CH_3}{CH}CH_2-,\quad -CH_2\underset{C_2H_5}{CH}CH_2CH_2,$$

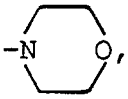


and

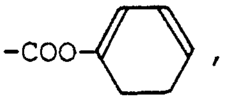


.

In the following, preferred examples as the water-soluble group represented by Rb_2 or a precursor thereof are shown. $-COOH$, $-COONa$, $-COOCH_3$, $-COOC_2H_5$, $-NHSO_2CH_3$, $-NHCOOCH_3$, $-NHCOOC_2H_5$, $-SO_3H$, $-SO_3K$, $-OH$,

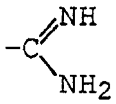


,



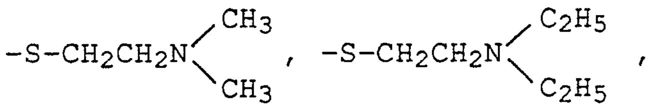
,

$-SO_2NH_2$,

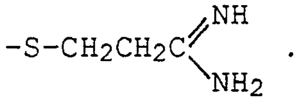


and $-NR_5'R_6'$ (where R_5' and R_6' each repersent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms).

As the bleaching accelerator group represented by $-S-Rb_1-Rb_2$, particularly preferred are $-S-CH_2CH_2COOH$, $-S-CH_2CH_2CH_2COOH$,

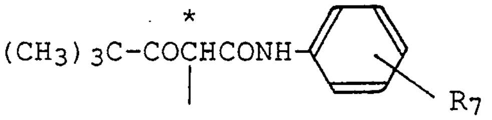


$$-S-CH_2CH_2N\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array},\quad -S-CH_2CH_2N\begin{array}{l}\diagup C_2H_5\\ \diagdown C_2H_5\end{array},$$

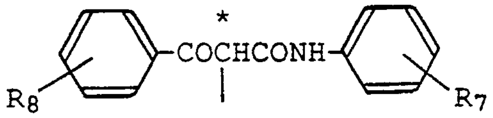


$$-S-CH_2CH_2C\begin{array}{l}\diagup\!\!\!\diagup NH\\ \diagdown NH_2\end{array}.$$

As the yellow coupler residue represented by Cp in the formulae (BAR-A) and (BAR-B), those represented by the following formulae (II) and (III) are preferred.



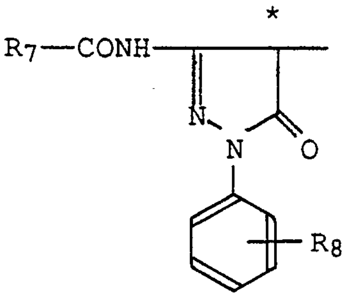
(II)



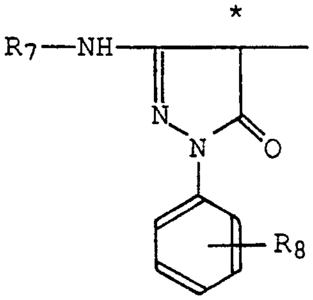
(III)

In the above formulae (II) and (III), R_7 and R_8 each represent an alkyl group, a cycloalkyl group, an aryl group, a hetero ring or a halogen atom, and the alkyl group, the cycloalkyl group, the aryl group and the hetero ring described above may be bonded through an oxygen atom, a nitrogen atom or a sulfur atom. Further, the alkyl group, the cycloalkyl group, the aryl group and the hetero ring described above may be bonded through the following bonding groups. Specifically, these groups may be bonded through each group of acylamino, carbamoyl, sulfonamide, sulfamoyl, sulfamoylcarbonyl,carbonyloxy, oxycarbonyl, ureido, thioureido, thioamide, sulfone and sulfonyloxy. Further, the alkyl group, the cycloalkyl group, the aryl group and the hetero ring described above may include those having substituent groups described below. Specifically, as said substituent groups, there may be mentioned, for example, a halogen atom, each group of nitro, cyano, alkyl, alkenyl, cycloalkyl, aryl, alkoxy, aryloxy, alkoxycarbonyl, aryloxycarbonyl, carboxy, sulfo, sulfamoyl, carbamoyl, acylamino, ureido, urethane, sulfonamide, hetero ring, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkylamino, anilino, hydroxy, imide and acyl. When two or more R_7 and R_8 are present, they may be the same or different.

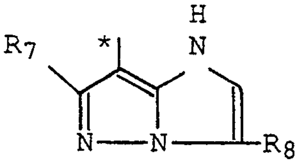
In the formulae (BAR-A) and (BAR-B), as the magenta coupler residue represented by Cp, those represented by the following formulae (IV), (V), (VI) and (VII) are preferred.



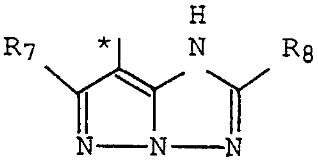
(IV)



(V)



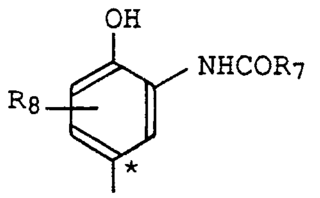
(VI)



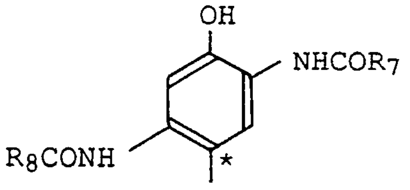
(VII)

In the above formulae (IV) to (VII), R_7 and R_8 have the same meanings as R_7 and R_8 in the formulae (II) and (III), respectively.

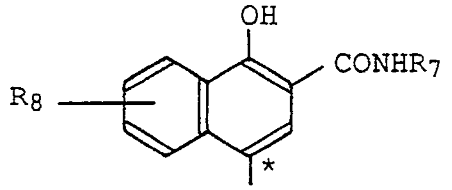
As the cyan coupler residue represented by Cp in the formulae (BAR-A) and (BAR-B), those represented by the following formulae (VIII), (IX) and (X) are preferred.



(VIII)



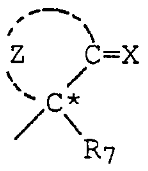
(IX)



(VIII)

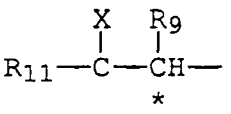
In the above formulae (VIII) to (X), R_7 and R_8 have the same meanings as R_7 and R_8 in the formulae (II) and (III), respectively.

As the coupler residue which forms a substantially colorless product, represented by Cp in the formulae (BAR-A) and (BAR-B), those represented by the formulae (XI) to (XIV) are preferred.



(XI)

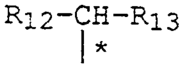
wherein R_9 represents a hydrogen atom, an alkyl group, an aryl group, a halogen atom, an alkoxy group, an acyloxy group or a heterocyclic group; X represents an oxygen atom or $=N\text{-}R_{10}$ where R_{10} represents an alkyl group, an aryl group, a hydroxy group, an alkoxy group or a sulfonyl group; and Z represents a group of non-metallic atoms necessary for forming 5- to 7-membered carbon rings (e.g. indanone, cyclopentanone and cyclohexanone) and hetero rings (e.g. piperidone, pyrrolidone and hydrocarbostyryl).



$$R_{11}-\overset{X}{\overset{|}{C}}-\underset{*}{\overset{R_9}{\overset{|}{CH}}}-$$

(XII)

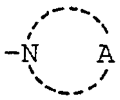
wherein R_9 and X have the same meanings as R_9 and X in the formula (XI), respectively; and R_{11} represents an alkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an alkylamino group, a dialkylamino group or an anilino group.



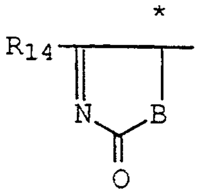
$$R_{12}-\underset{|\,*}{CH}-R_{13}$$

(XIII)

wherein R_{12} and R_{13} may be the same or different, and each represent an alkoxycarbonyl group, a carbamoyl group, an acyl group, a cyano group, a formyl group, a sulfonyl group, a sulfinyl group, a sulfamoyl group, an ammonium group or



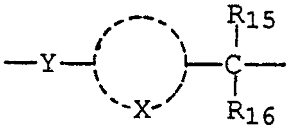
where A represents a group of non-metallic atoms necessary for forming 5- to 7-membered hetero rings (e.g. phthalimide, triazole and tetrathiazole) with a nitrogen atom.



(XIV)

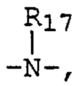
wherein R_{14} represents, for example, an alkyl group, an aryl group, an anilino group, an alkylamino group or an alkoxy group; and B represents an oxygen atom, a sulfur atom or a nitrogen atom.

The TIME useful for practicing the present invention may include those represented by the following formulae (XV), (XVI) and (XVII), but the present invention is not limited to these.



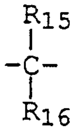
(XV)

wherein X represents a benzene ring which may have a substituent group or a group of atoms necessary for forming a naphthalene ring; Y represents -O-, -S- or



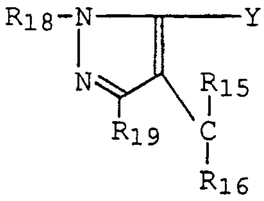
$$-\overset{R_{17}}{\overset{|}{N}}-,$$

and is bonded to a coupling position of the coupler residue represented by Cp in the formulae (BAR-A) and (BAR-B); R_{15}, R_{16} and R_{17} each represent a hydrogen atom, an alkyl group or an aryl group; and a



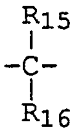
$$-\overset{R_{15}}{\overset{|}{\underset{R_{16}}{\underset{|}{C}}}}-$$

group is substituted with Y at an ortho-position or a para-position, and bonded to an oxygen atom of a bleaching accelerator group.



(X-VI)

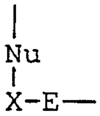
wherein Y, R_{15} and R_{16} have the same meanings of those in the formula (XV), respectively; R_{18} represents, for example, a hydrogen atom, an alkyl group, an aryl group, an acyl group, a sulfonyl group, an alkoxycarbonyl group and a heterocyclic residue; R_{19} represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic residue, an alkoxy group, an amino group, an acid amide group, a sulfonamide group, a carboxy group, an alkoxycarbonyl group, a carbamoyl group and a cyano group; and this timing group is bonded to a coupling position of the coupler residue represented by Cp in the formulae (BAR-A) and (BAR-B) by Y similarly as in the formula (XV), and to an oxygen atom of a bleaching acceralator group by a



$$-\overset{R_{15}}{\underset{R_{16}}{C}}-$$

group.

Next, an example of the timing group which releases a bleaching accelerator group by the intermolecular nucleophilic substitution reaction is represented by the formula (XVII).

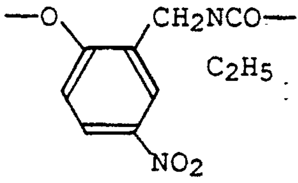


$$\overset{|}{\underset{|}{Nu}}$$
$$X\text{-}E\text{—}$$

(XVII)

wherein Nu is a nucleophilic group having an oxygen, sulfur or nitrogen atom abundant in electrons, and bonded to a coupling position of the coupler residue represented by Cp in formulae (BAR-A) and (BAR-B); E is an electrophilic group having a carbonyl group, a thiocarbonyl group, a phosphinyl group or a thiophosphinyl group insufficient in electrons, and bonded to an oxygen atom of a bleaching accelerator group; and X makes a stereographic relationship between Nu and E, and is a bonding group which undergoes the intermolecular nucleophilic substitution reaction accompanied with formation of a 3-membered ring or a 7-membered ring after Nu is released from the coupler residue represented by Cp in the formulae (BAR-A) and (BAR-B), and thereby can release a bleaching accelerator.

Representative specific examples of the timing group may include the following compounds.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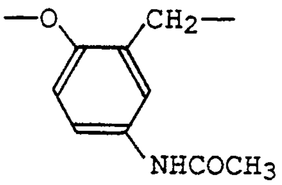
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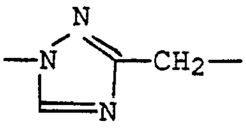
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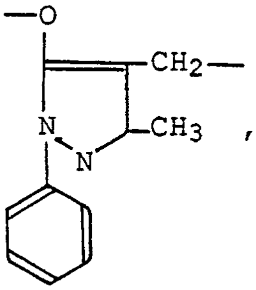
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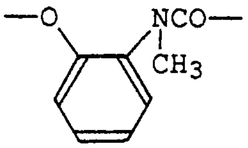
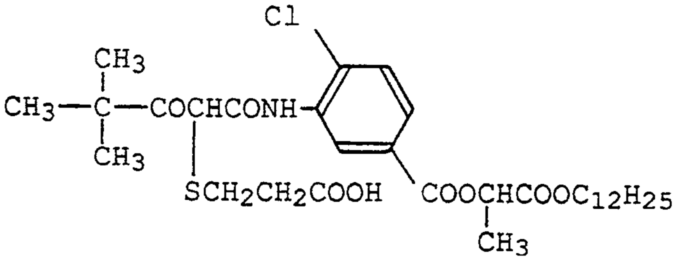
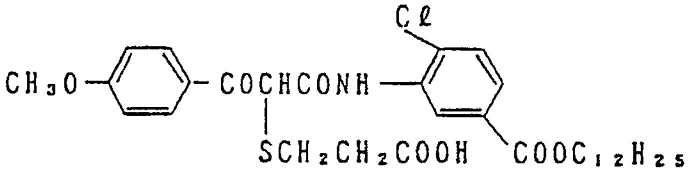

and —OCH$_2$CH$_2$NHCO— .

In the following, specific examples of the BAR compound which can be used in the present invention are shown, but the present invention is not limited to these examples.

(1)



(2)



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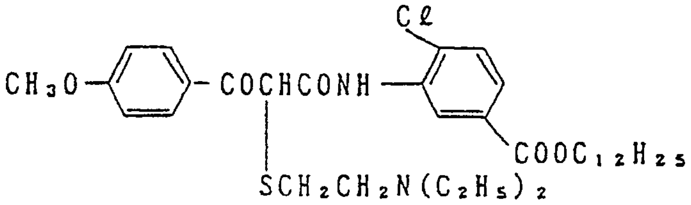

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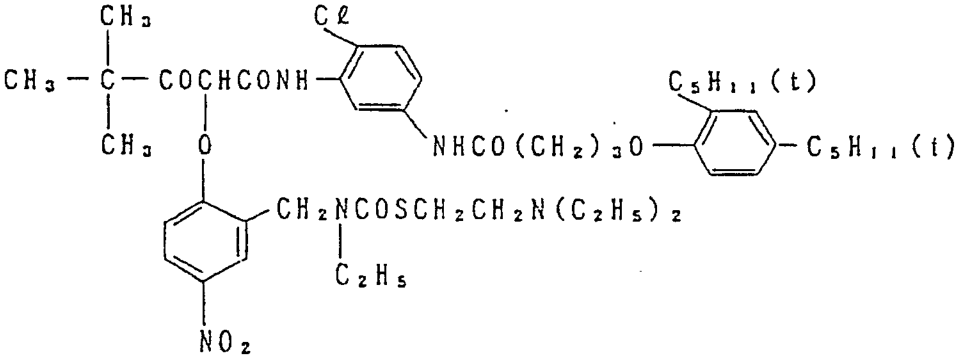

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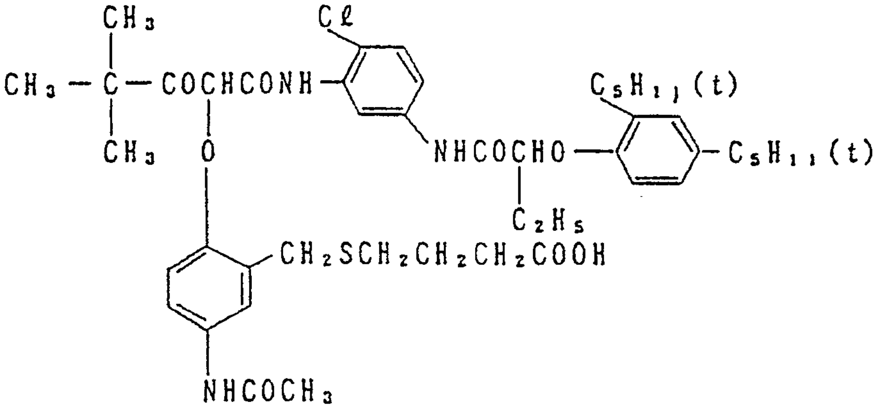

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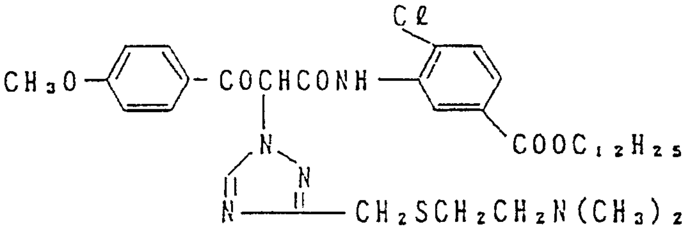

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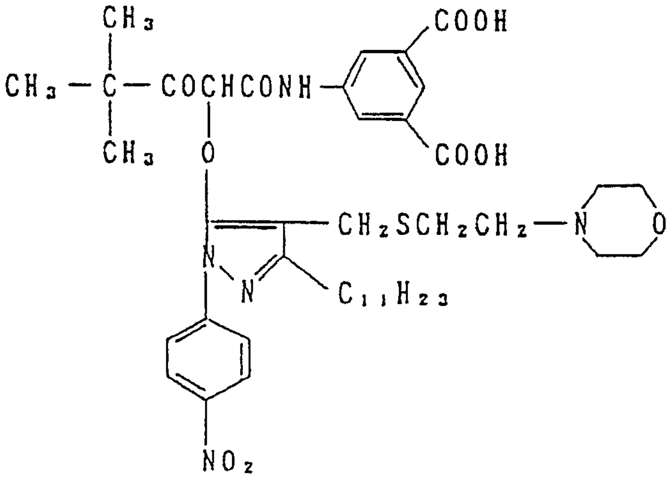

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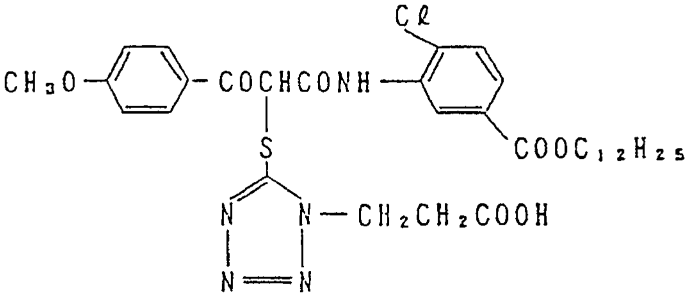

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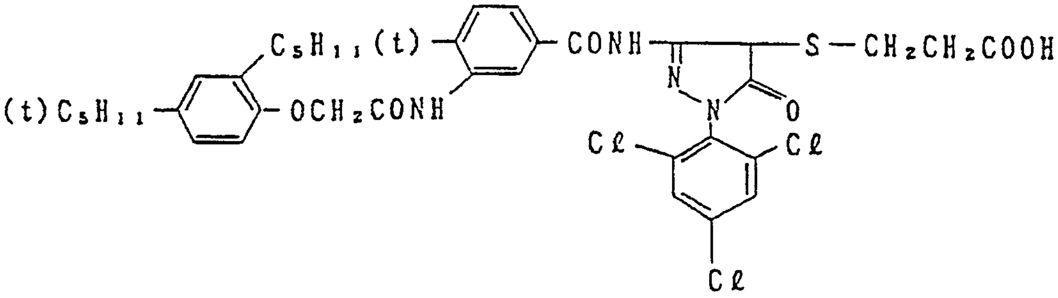
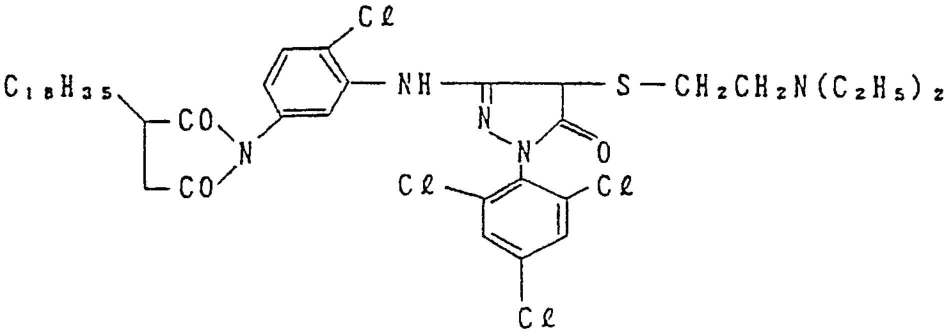
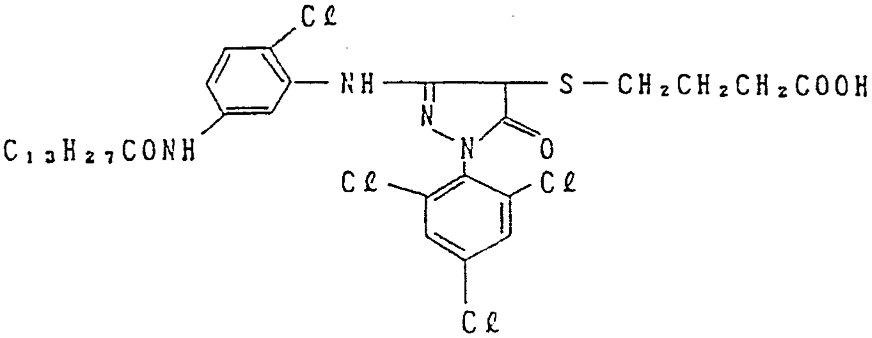

C5H11(t)
(t)C5H11
OCH2CONH
CONH
S—CH2CH2COOH
N
N
O
Cℓ
Cℓ
Cℓ

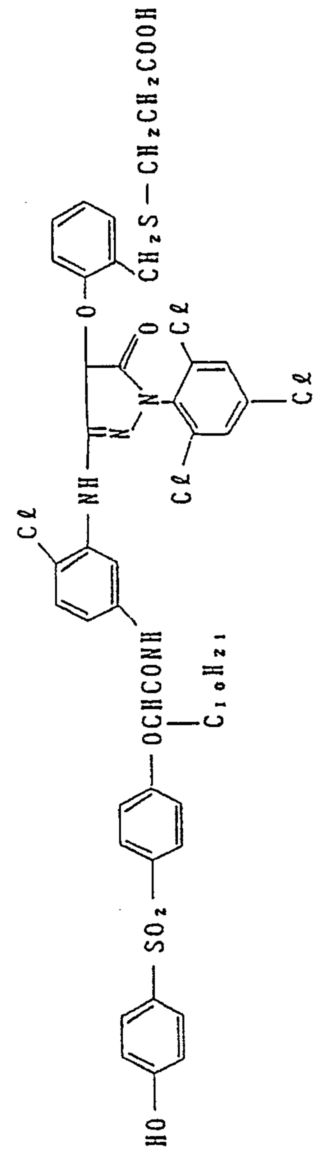
(10)


Cℓ
C18H35
CO
N
CO
NH
S—CH2CH2N(C2H5)2
N
N
O
Cℓ
Cℓ
Cℓ

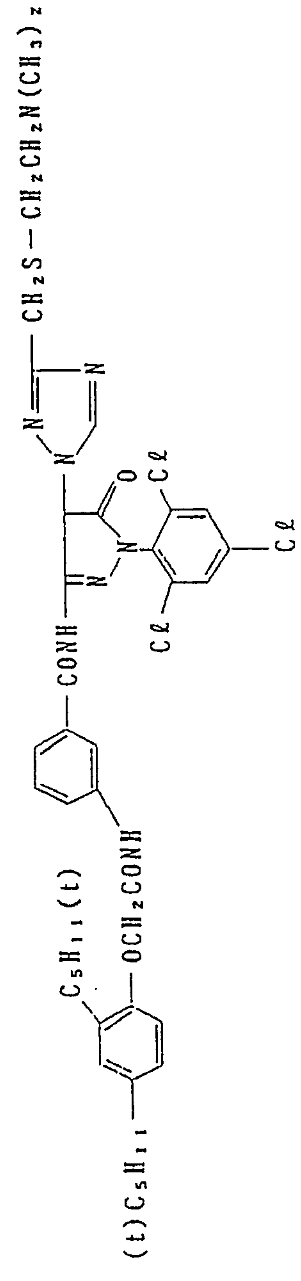
(11)


Cℓ
C13H27CONH
NH
S—CH2CH2CH2COOH
N
N
O
Cℓ
Cℓ
Cℓ

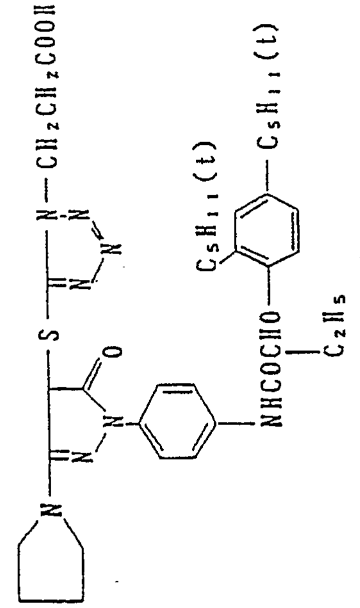
(12)



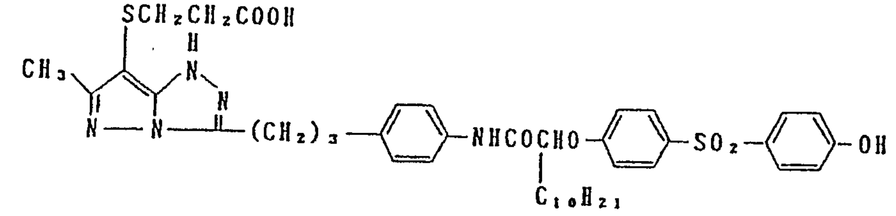
(13)



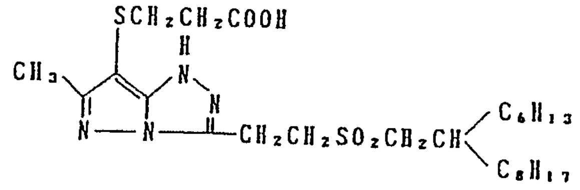
(14)



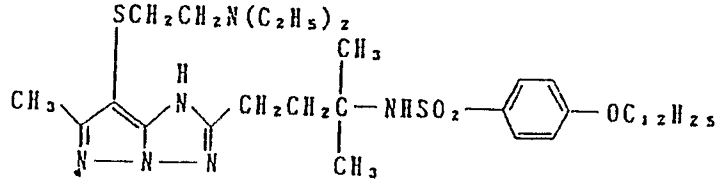
(15)



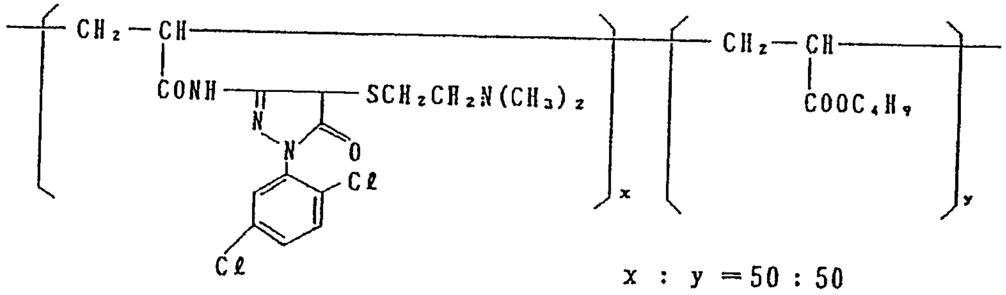
(16)



(17)

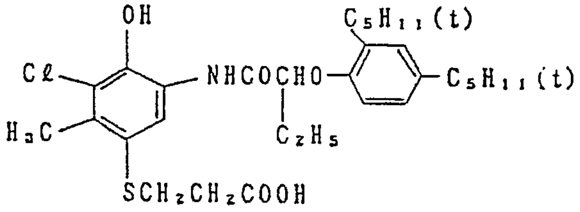


(18)

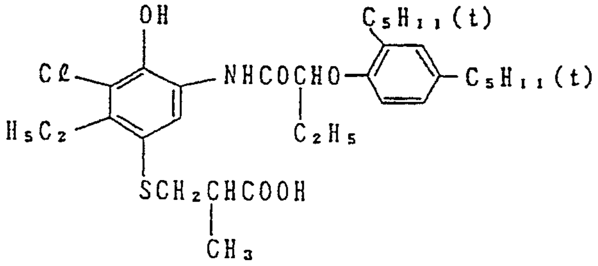


x : y = 50 : 50

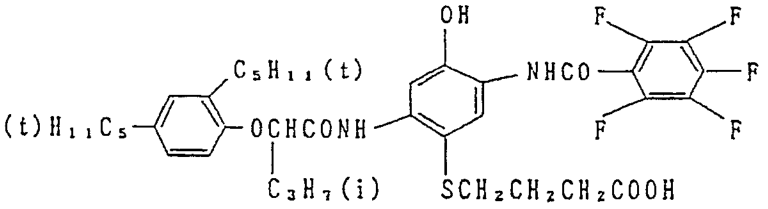
(19)



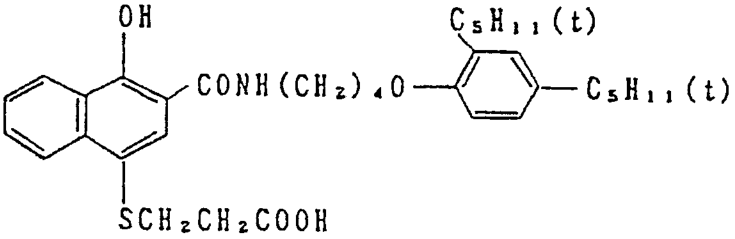
(20)



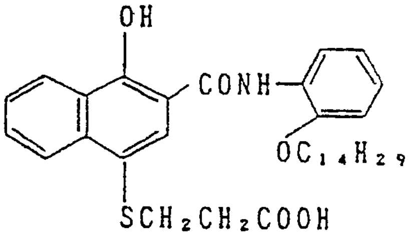
(21)



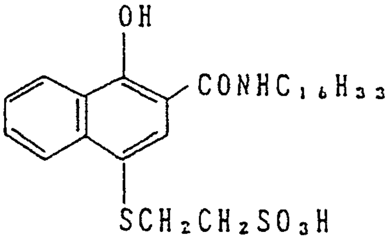
(22)



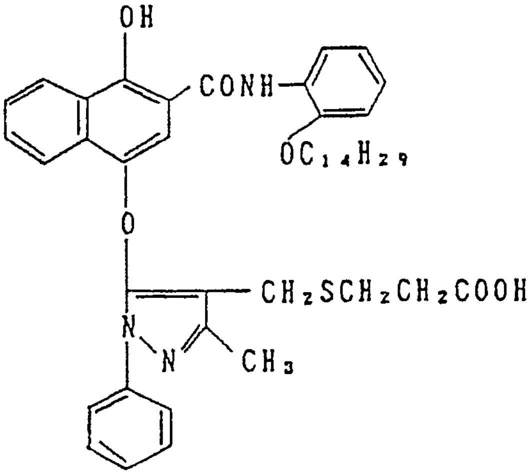
(23)



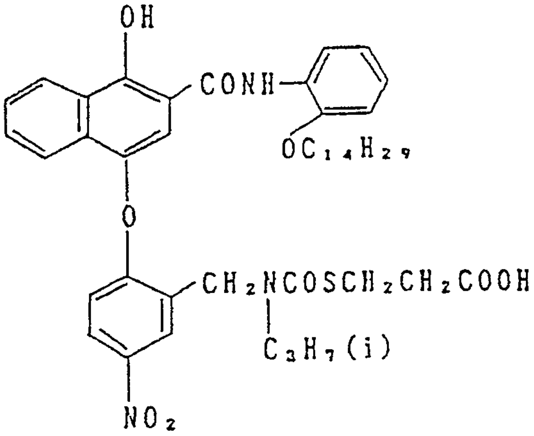
(24)



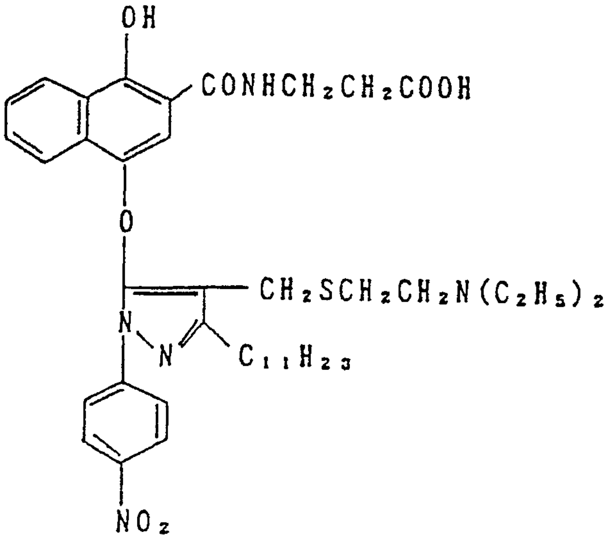
(25)


OH
CONH
OC14H29
O
CH2SCH2CH2COOH
N
N
CH3

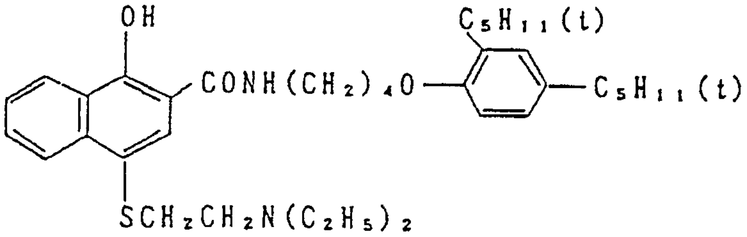
(26)


OH
CONH
OC14H29
O
CH2NCOSCH2CH2COOH
C3H7(i)
NO2

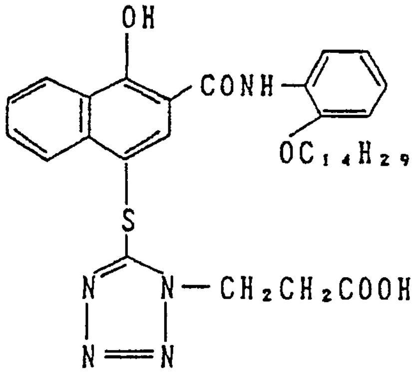
(27)


OH
CONHCH₂CH₂COOH
O
CH₂SCH₂CH₂N(C₂H₅)₂
N
N
C₁₁H₂₃
NO₂

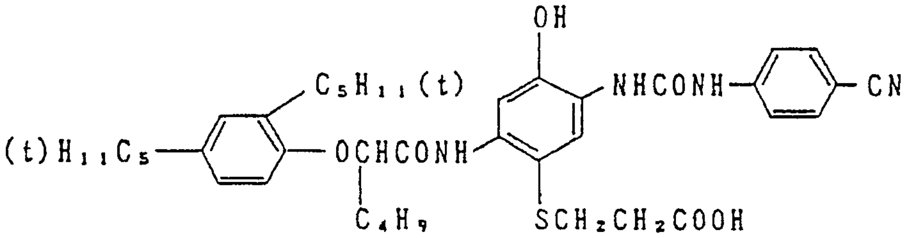
(28)


OH
CONH(CH₂)₄O
C₅H₁₁(t)
C₅H₁₁(t)
SCH₂CH₂N(C₂H₅)₂

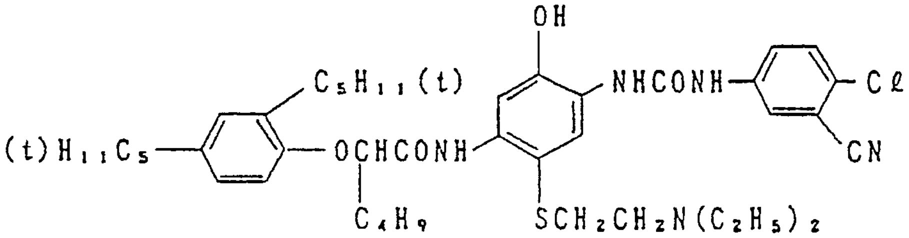
(29)


OH
CONH
OC₁₄H₂₉
S
N
N—CH₂CH₂COOH
N═N

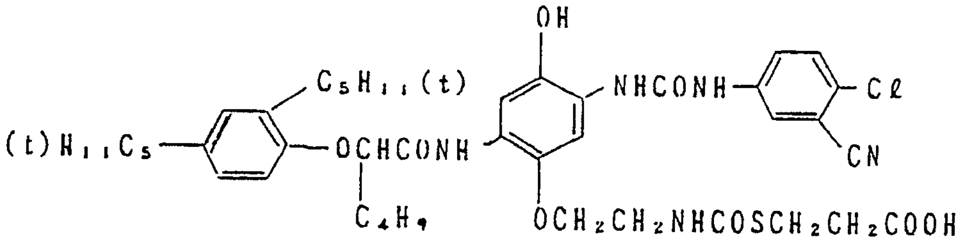
(30)


OH
C₅H₁₁(t)
NHCONH
CN
(t)H₁₁C₅
OCHCONH
C₄H₉
SCH₂CH₂COOH

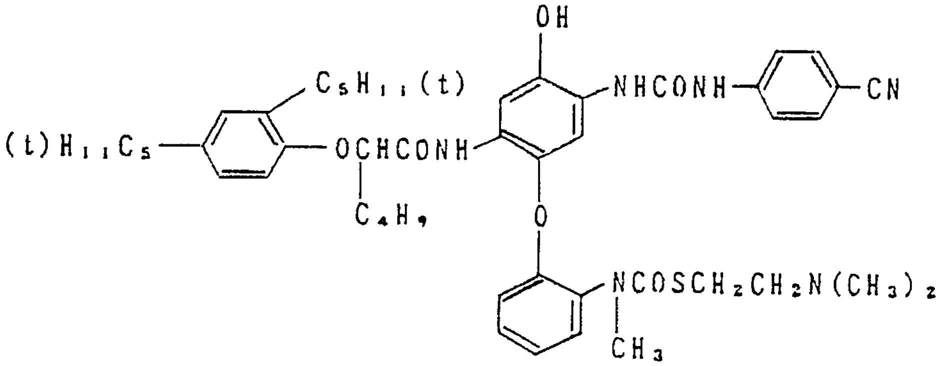
(31)


OH
C₅H₁₁(t)
NHCONH
Cℓ
CN
(t)H₁₁C₅
OCHCONH
C₄H₉
SCH₂CH₂N(C₂H₅)₂

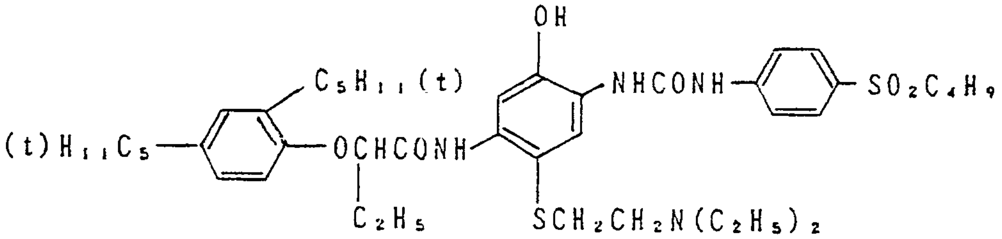
(32)



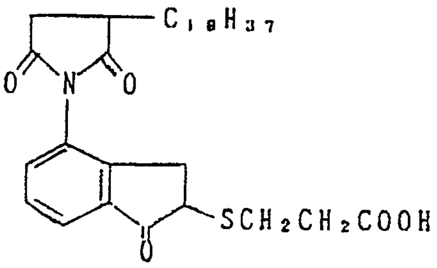
(33)



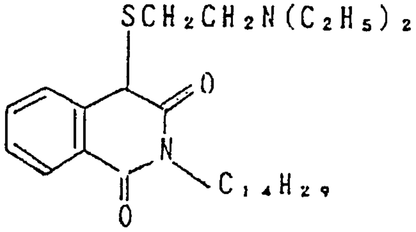
(34)



(35)

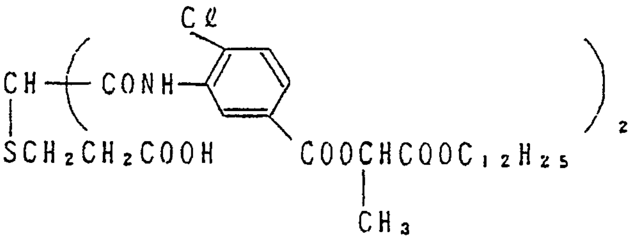


(36)

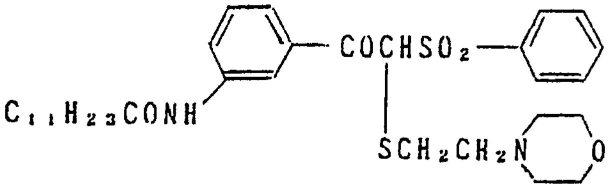


(37)

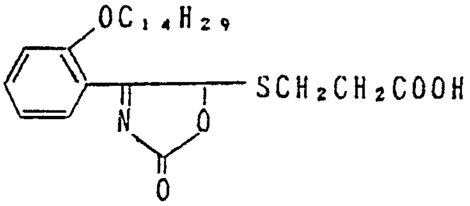
(38)



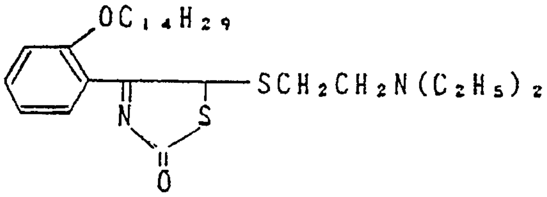
(39)


$C_{11}H_{23}CONH$
$COCHSO_2$
SCH_2CH_2N
O

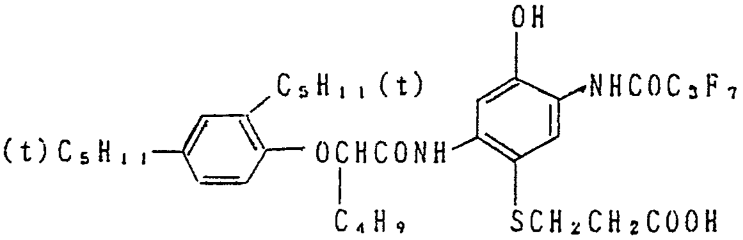
(40)


$OC_{14}H_{29}$
SCH_2CH_2COOH
N
O
O

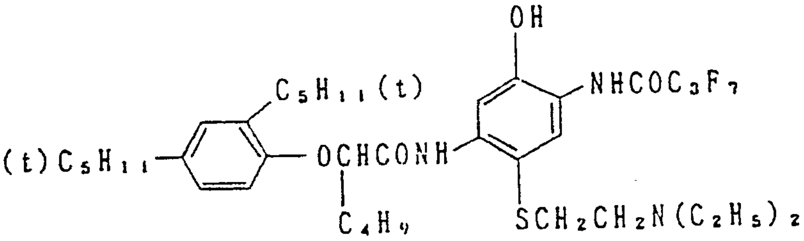
(41)


$OC_{14}H_{29}$
$SCH_2CH_2N(C_2H_5)_2$
N
S
O

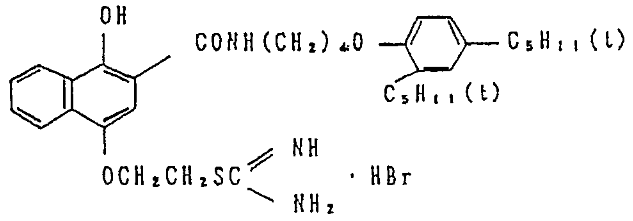
(42)


OH
$C_5H_{11}(t)$
$NHCOC_3F_7$
$(t)C_5H_{11}$
OCHCONH
C_4H_9
SCH_2CH_2COOH

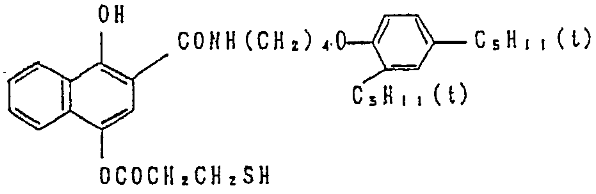
(43)


OH
$C_5H_{11}(t)$
$NHCOC_3F_7$
$(t)C_5H_{11}$
OCHCONH
C_4H_9
$SCH_2CH_2N(C_2H_5)_2$

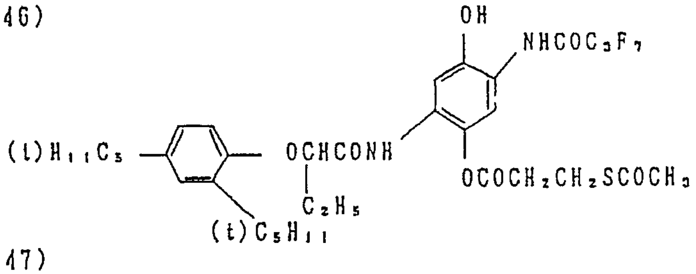
(44)



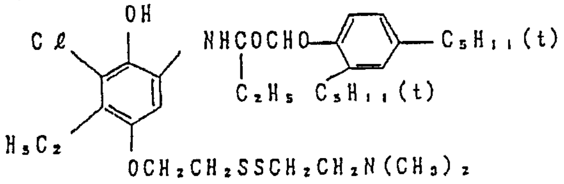
(45)



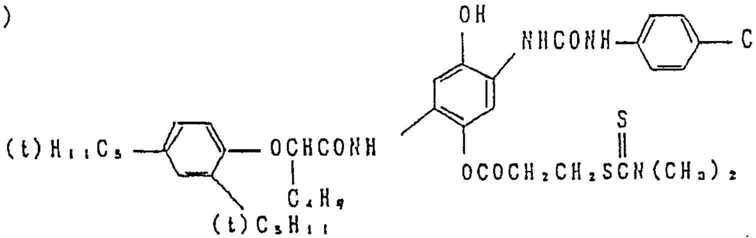
(46)



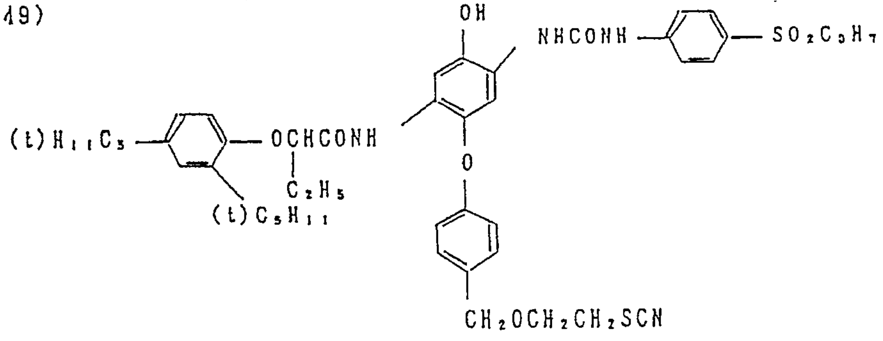
(47)



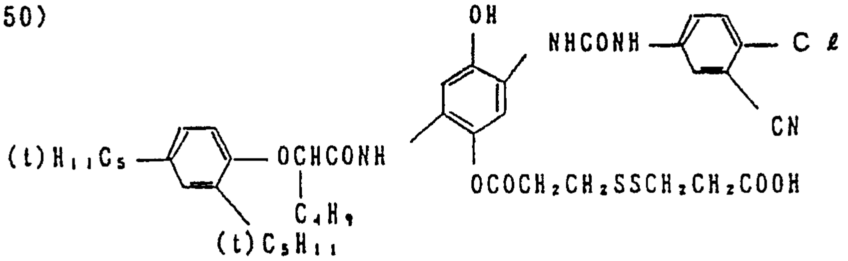
(48)



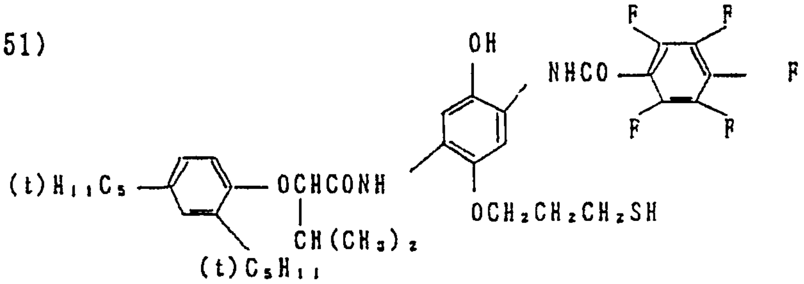
(49)



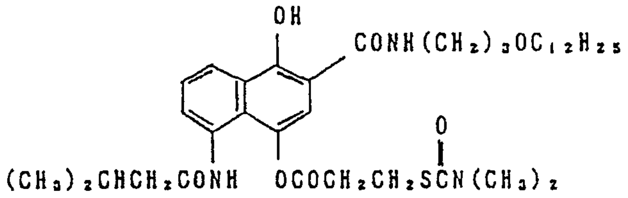
(50)



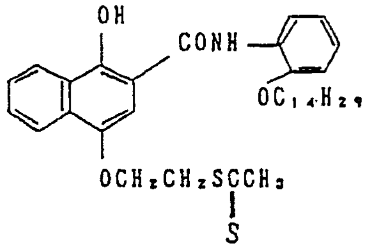
(51)



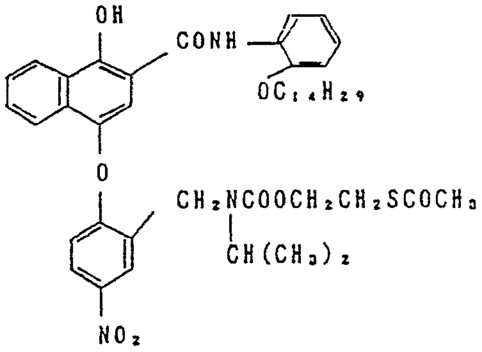
(52)



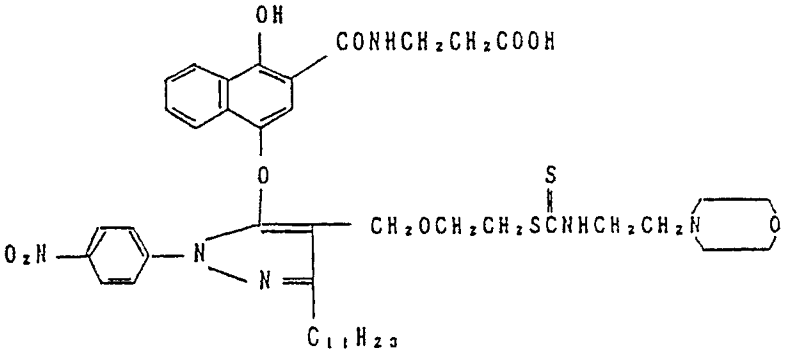
(53)



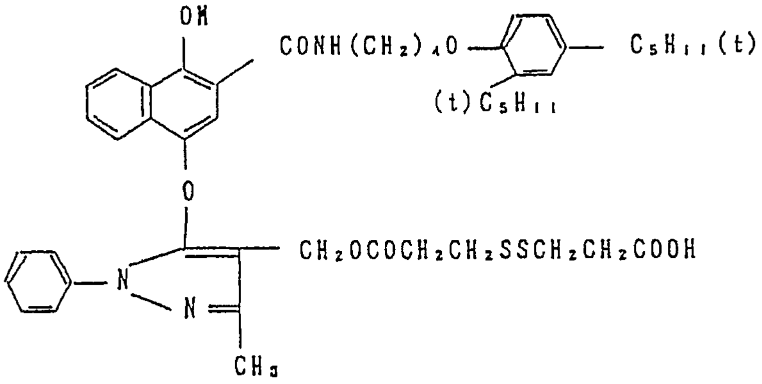
(54)



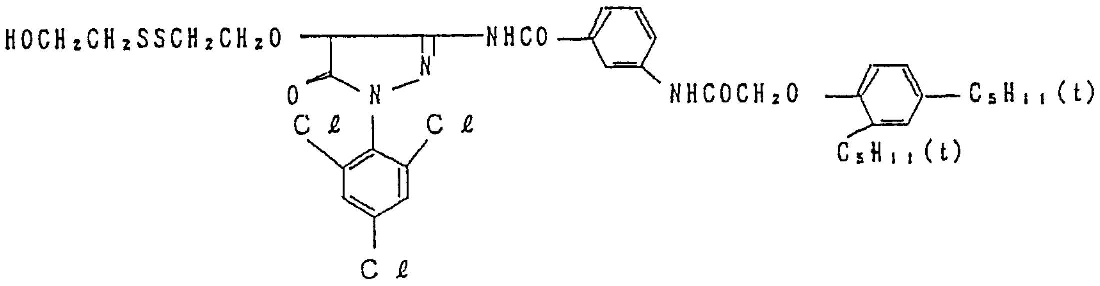
(55)



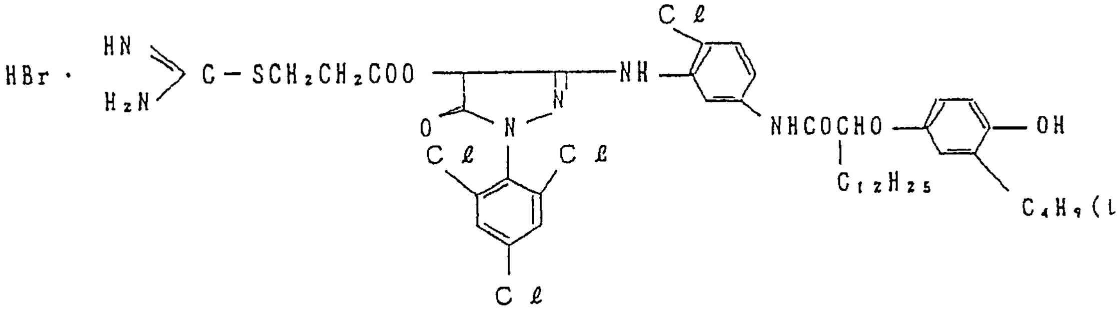
(56)


OH
CONH(CH2)4O
C5H11(t)
(t)C5H11
O
CH2OCOCH2CH2SSCH2CH2COOH
N
N
CH3

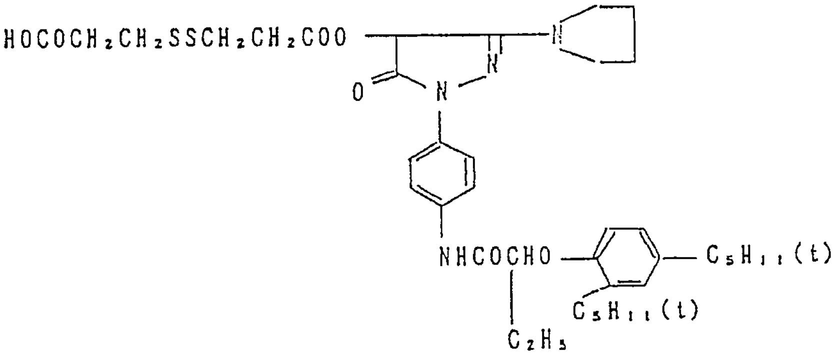
(57)


HOCH2CH2SSCH2CH2O
NHCO
N
O
N
NHCOCH2O
C5H11(t)
C5H11(t)
Cℓ
Cℓ
Cℓ

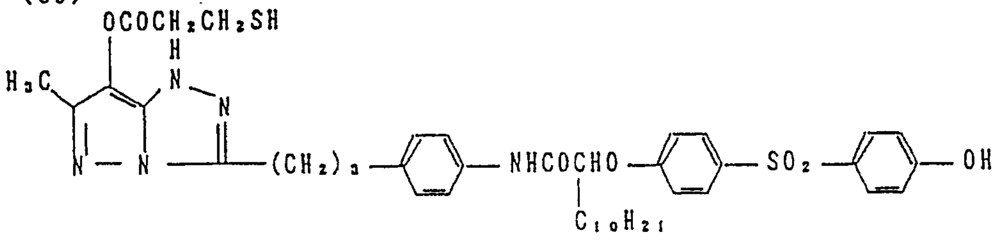
(58)


Cℓ
HN
HBr ·
H2N
C − SCH2CH2COO
NH
N
O
N
NHCOCHO
OH
C12H25
C4H9(t
Cℓ
Cℓ
Cℓ

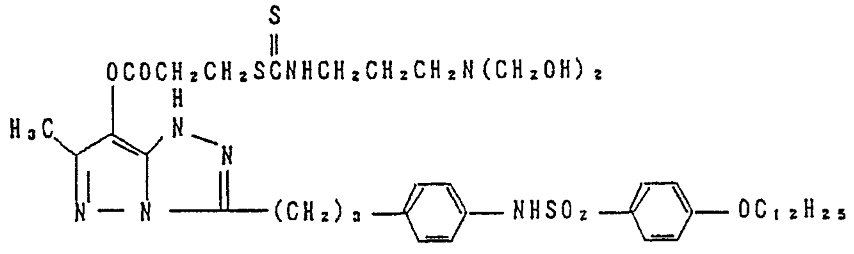
(59)


HOCOCH2CH2SSCH2CH2COO
N
N
O
N
NHCOCHO
C5H11(t)
C5H11(t)
C2H5

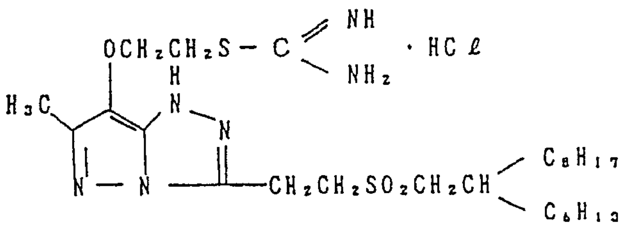
(60)



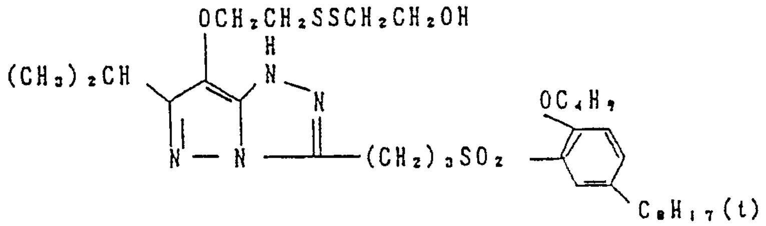
(61)



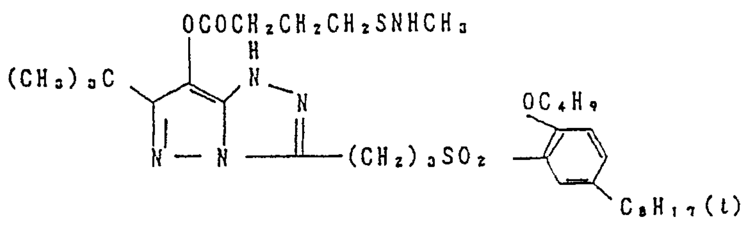
(62)



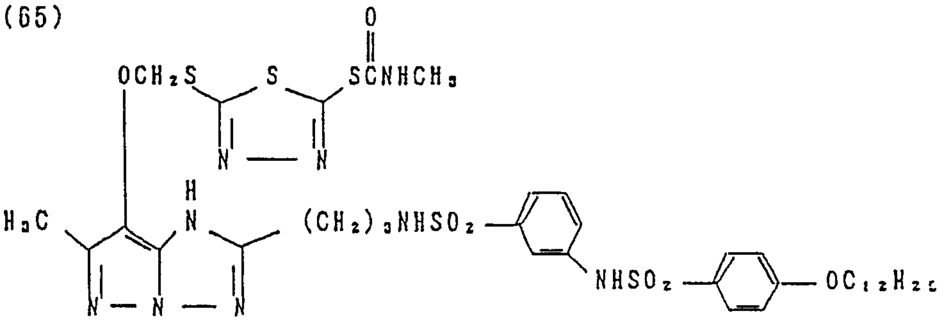
(63)



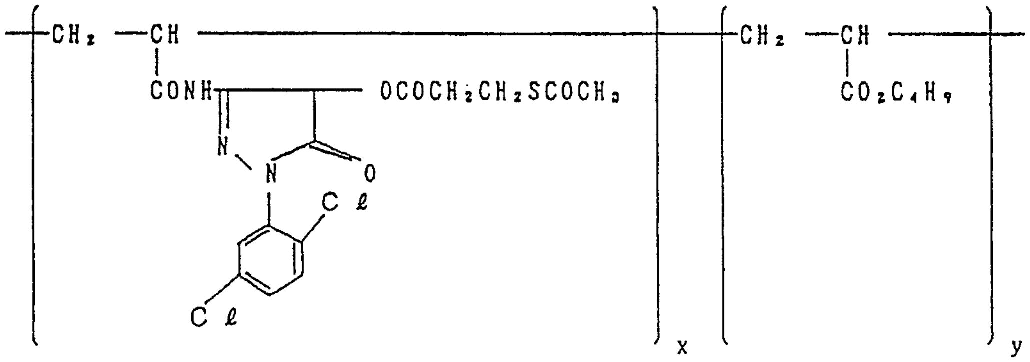
(64)



(65)

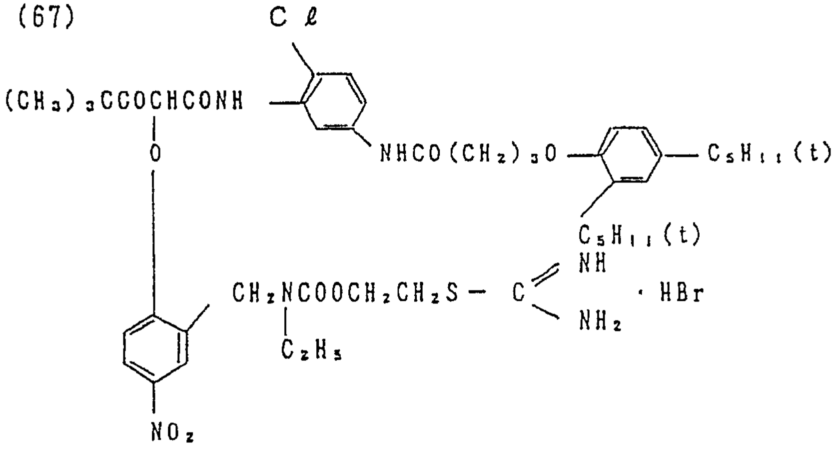


(66)

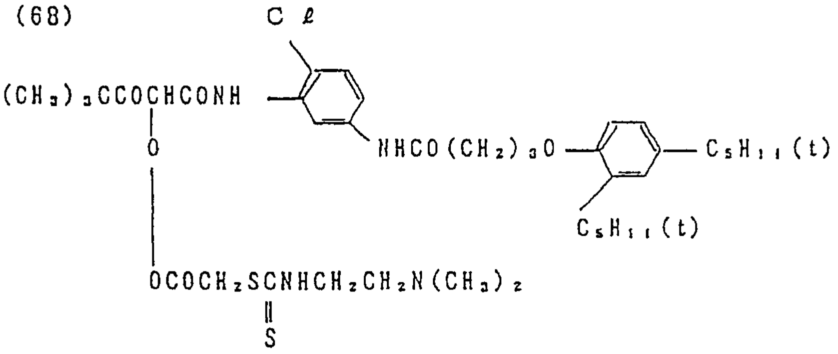


x : y = 50 : 50

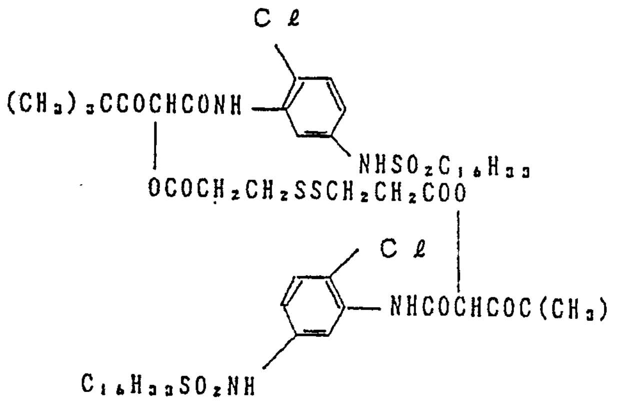
(67)



(68)

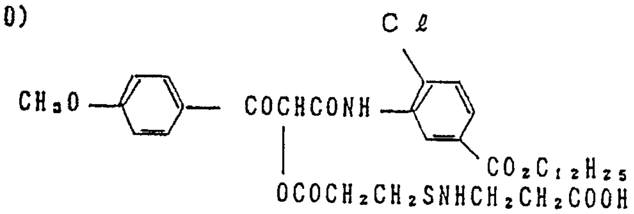


(69)



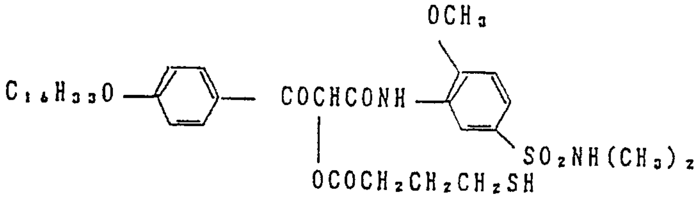
Cℓ
(CH3)3CCOCHCONH
NHSO2C16H33
OCOCH2CH2SSCH2CH2COO
Cℓ
NHCOCHCOC(CH3)
C16H33SO2NH

(70)



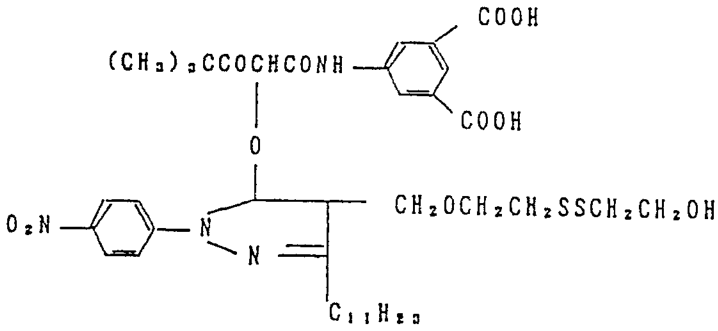
Cℓ
CH3O
COCHCONH
CO2C12H25
OCOCH2CH2SNHCH2CH2COOH

(71)



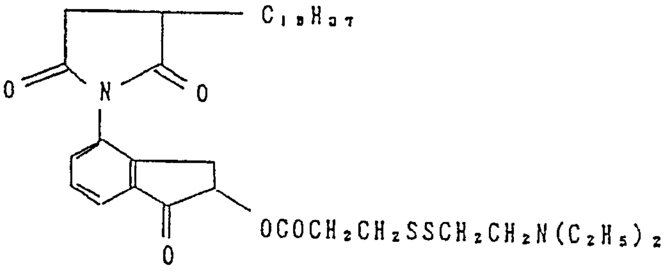
OCH3
C16H33O
COCHCONH
SO2NH(CH3)2
OCOCH2CH2CH2SH

(72)



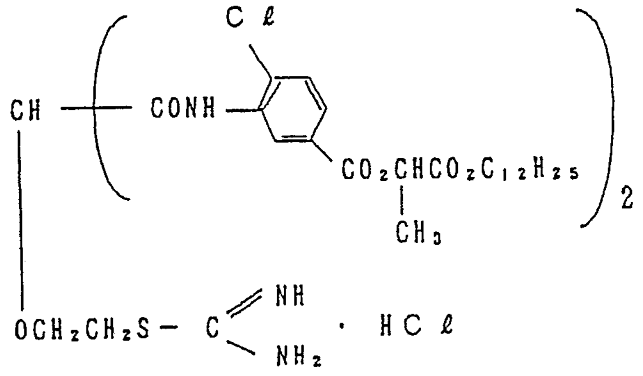
COOH
(CH3)3CCOCHCONH
COOH
O
CH2OCH2CH2SSCH2CH2OH
O2N
N
N
C11H23

(73)

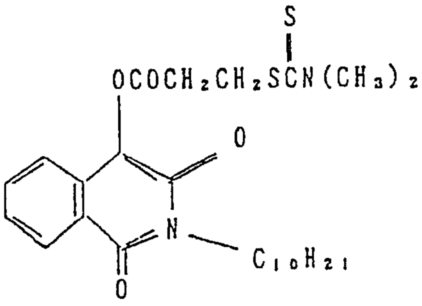


C18H37
O
N
O
O
OCOCH2CH2SSCH2CH2N(C2H5)2

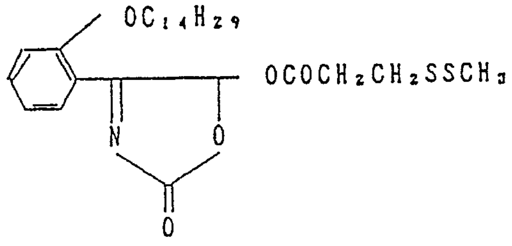
(74)



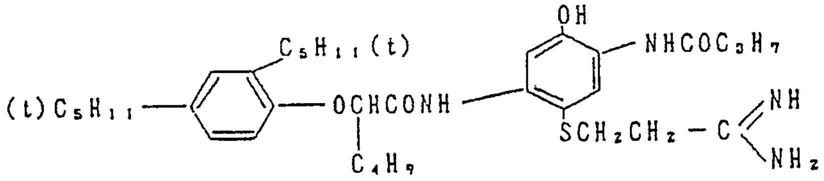
(75)



(76)



(77)



In the method for processing the light-sensitive silver halide color photographic material of the present invention, as a silver halide emulsion to be used in the light-sensitive material for negative images, there may be preferred a silver halide emulsion containing silver halide grains which are constituted of two or more phases having different silver iodide contents, and have said average silver iodide content higher than the silver iodide content of a peripheral phase thereof.

The state that the average silver iodide content of the grains is higher than the silver iodide content of the peripheral phase of the grains can be measured according to the following method.

When the silver halide emulsion is an emulsion containing silver halide grains having an average value of grain size/grain thickness of less than 5, an average silver iodide content (J_1) obtained by an X-ray fluorescence analysis and a silver iodide content of a grain surface (J_2) obtained by an X-ray excited photoelectron spectroscopy are compared, the relationship of $J_1>J_2$ is satisfied.

The grain size herein mentioned is a diameter of a circumscribed circle of a plane which has a maximum projected area of the grain.

The X-ray excited photoelectron spectroscopy is explained.

Prior to a measurement by the X-ray excited photoelectron spectroscopy, an emulsion is pretreated in the following manner. First, a pronase solution is added to the emulsion, and stirred at 40 °C for 1 hour to effect gelatin degradation. Subsequently, after centrifugation was carried out to precipitate emulsion grains, a supernatant was removed, and then an aqueous pronase solution was added to effect gelatin degradation again under the above conditions. This sample was subjected again to centrifugation, a supernatant was removed, and then distilled water was added to redisperse the emulsion grains in distilled water, followed by centrifugation and removal of a supernatant. After this washing operation was repeated three times, the emulsion grains were redispersed in ethanol. The solution obtained was coated thinly on a silicone wafer applied with mirror polishing to give a sample for measurement.

In the measurement according to the X-ray excited photoelectric spectroscopy, ESCA/SAM Model 560 (trade name) manufactured by PHI Co. is used as a device, and the measurement is conducted under the conditions of X-rays for excitation of Mg-Kα rays, an X-ray source voltage of 15 KV, an X-ray source current of 40 mA and a pass energy of 50 eV.

For measuring a surface halide composition, Ag_3d, Br_3d and $I_3d_3/_2$ elecrons are detected.

A composition ratio is calculated by using integral intensities of the respective peaks according to the relative sensitivity coefficient method. As the relative sensitivity coefficients of Ag3d, Br3d and I3d3/2, 5.10, 0.81 and 4.592 are used, respectively, thereby giving a composition ratio in a unit of atomic percentage.

When the silver halide emulsion to be used in the present invention contains grains having an average value of grain size/grain thickness of less than 5, a grain size distribution is preferably monodispersed. The monodispersed silver halide emulsion refers to an emulsion in which a weight of silver halide included within the range of ± 20 % of its grain size with an average grain size $\bar{r}$ as a center is 60 % or more, preferably 70 % or more, more preferably 80 % or more of a total weight of silver halide grains.

Here, the average grain size $\bar{r}$ is defined as a grain size ri when the product of ni which is frequency of grains having a grain size of ri and ri^3 (ni x ri^3) becomes maximum (effective number of 3 digits, a number of a minimum digit is rounded).

When the silver halide grain is spherical, the grain size mentioned here is its diameter, and when the silver halide grain has a shape other than sphere, it is a diameter obtained by converting its projected area to a circle area having the same area.

The grain size can be obtained by, for example, photographing said grains magnified at a magnification of 10,000 to 50,000 with an electron microscope, and by measuring a diameter or a projected area of the grains on the print (there should be randomly 1,000 or more grains to be measured on the print).

The highly monodispersed emulsion particularly preferred in the present invention is an emulsion having a distribution width of 20 % or less, preferably 15 % or less defined by the following formula:

$$\frac{\text{Standard deviation}}{\text{Average grain size}} \times 100 = \text{Distribution width (\%)}$$

Here, the average grain size and the standard deviation of the grains are determined from ri defined above.

In the case where the silver halide emulsion is a tabular silver halide emulsion having an average value of grain size/grain thickness of 5 or more, when an average silver iodide content (J) obtained by the above X-ray fluorescence analysis and an average measured value of a silver iodide content measured on silver halide crystals which are apart by 80 % or more from a central portion relative to a grain size direction of the silver halide grains (J_3) according to an X-ray microanalysis are compared, the relationship of $J_1>J_3$ is satisfied.

The X-ray microanalysis is explained. In a grid for observation with a electron microscope in which an energy dispersion type X-ray analysis device is provided, silver halide grains are dispersed, and a magnification is set by cooling with liquid nitrogen so that there is one grain within a CRT field, and intensities of ILα rays and AgLα rays for a predetermined time are integrated. By using an intensity ratio of ILα/AgLα and a calibration curve previously prepared, a silver iodide content can be calculated.

In the tabular silver halide emulsion having an average value of grain size/grain thickness of 5 or more, the average value of grain size/grain thickness is preferably 6 or more and 100 or less, particularly preferably 7 or more and 50 or less.

In the silver halide emulsion having an average value of grain size/grain thickness of less than 5 of the present invention, the silver iodide content of the grain surface measured according to the X-ray excited photoelectron spectroscopy is preferably 6 to 0 mole %, more preferably 5 to 0 mole %, particularly preferably 4 to 0.01 mole %.

In the tabular silver halide emulsion having an average value of grain size/grain thickness of 5 or more of the present invention, the average measured value of a silver iodide content measured on silver halide crystals which are apart by 80 % or more from a central portion relative to a grain size direction of the silver halide grains (J_3) according to the X-ray microanalysis is preferably 6 to 0 mole %, more preferably 5 to 0 mole %, particularly preferably 4 to 0.01 mole %. The average thickness of the tabular silver halide grains is preferably 0.5 to 0.01 μm, particularly preferably 0.3 to 0.05 μm. The average grain size of the silver halide grains contained in the tabular silver halide emulsion is preferably 0.5 to 30 μm, more preferably 1.0 to 20 μm.

The above silver halide emulsion having an average value of grain size/grain thickness of less than 5 is preferably monodispersed, and preferably of a core/shell type. The above tabular silver halide emulsion having an average value of grain size/grain thickness of 5 or more comprises preferably silver iodide existing locally at a central portion of the grain.

The core/shell type silver halide emulsion having an average value of grain size/grain thickness of less than 5 comprises silver halide grains having a grain structure comprising two or more phases having different silver iodide contents, in which a phase with the highest silver iodide content (called "core") is not the most outer layer (called "shell").

In the inner phase with the highest silver iodide content (core), the silver iodide content is preferably 6 to 40 mole %, more preferably 8 to 30 mole %, particularly preferably 10 to 20 mole %. The silver iodide content of the most outer phase is preferably less than 6 mole %, more preferably 0 to 4.0 mole %.

The rate of the shell portion in the core/shell type silver halide grains is preferably 10 to 80 %, more preferably 15 to 70 %, particularly preferably 20 to 60 % in volume.

The rate of the core portion is preferably 10 to 80 %, more preferably 20 to 50 % in volume of the total grains.

The difference between the core portion with a high silver iodide content and the shell portion with a low silver iodide content may have a sharp borderline or may change continuously without a distinct borderline. Also, silver halide grains having an intermediate phase with an intermediate silver iodide content between the contents of the core portion and the shell portion, between the core and the shell are preferably used.

When the silver halide emulsion comprises core/shell type silver halide grains having the above intermediate layer, the volume of the intermediate layer is preferably 5 to 60 %, more preferably 20 to 55 % of the total grains. The differences in silver iodide content between the shell and the intermediate layer and between the intermediate layer and the core are preferably 3 mole % or more, respectively, and the difference in silver iodide content between the shell and the core is preferably 6 mole % or more.

The core/shell type silver halide emulsion is preferably silver iodobromide, and its average silver iodobromide content is preferably 4 to 20 mole %, more preferably 5 to 15 mole %. Further, silver chloride can be contained within the range which does not impair the effect of the present invention.

The core/shell type silver halide emulsion can be prepared according to the known methods disclosed in Japanese Unexamined Patent Publications No. 177535/1984, No. 138538/1985, No. 52238/1984, No. 143331/1985, No. 35726/1985 and No. 258536/1985.

When the core/shell type silver halide emulsion is grown from seed grains as in the method disclosed in Example of Japanese Unexamined Patent Publication No. 138538/1985, there may be a halogen composition region which is different from the core in the central portion of the grains.

In such a case, as a halogen composition of the seed grains, there can be used any desired composition such as silver bromide, silver iodobromide, silver chloroiodobromide, silver chlorobromide and silver chloride, preferably silver iodobromide or silver bromide having a silver iodide content of 10 mole % or less.

The rate of the seed grains in total silver halide is preferably 50 % or less, particularly preferably 10 % or less in volume.

The distribution state of silver iodide in the above core/shell type silver halide grains can be detected according to various physical measurement methods. For example, it can be determined according to a luminescence measurement at low temperatures and an X-ray diffractometry as described in Summary of Lectures in Meeting of Japan Photographic Society in 1981.

The core/shell type silver halide grains may comprise either normal crystals which are cubic, tetradecahedral or octahedral or twins, and further it may comprise a mixture of these, but preferably normal crystals.

In the tabular silver halide emulsion having an average value of grain size/grain thickness of 5 or more and comprising silver iodide existing locally at a central portion of the grain, the phase with a high iodine content at the central portion is preferably 80 % or less, particularly 60 % to 10 % of the total volume. The silver iodide content at the central portion is preferably 5 to 40 mole %, particularly preferably 10 to 30 mole %. The phase with a low iodine content with which the phase with a high iodine content at the central portion is surrounded (a peripheral portion) may comprise silver iodobromide preferably having a silver iodide content of 0 to 10 mole %, more preferably 0.1 to 6.0 mole %.

The tabular silver halide emulsion comprising silver iodide existing locally at the central portion can be obtained by the known method disclosed in Japanese Unexamined Patent Publication No. 99433/1984.

In the method for processing the light-sensitive silver halide color photographic material of the present invention, the average silver iodide content of all the silver halide emulsions in the light-sensitive silver halide photographic material for negative images is preferably 0.1 to 15 mole %, more preferably 0.5 to 12 mole %, particularly preferably 1 to 6 mole %.

The average grain size of all the silver halide emulsions in the light-sensitive silver halide color photographic material for negative images is 2.0 μm or less, more preferably 0.1 to 1.0 μm or less, particularly preferably 0.2 to 0.6 μm.

The lower limit of the sum of total dry film thickness of all the hydrophilic colloid layers of the light-sensitive silver halide color photographic material for negative images (hereinafter described as "the film thickness of the emulsion surface") is limited depending on silver halide emulsions, couplers, lubricants and additives contained therein, and the film thickness of the emulsion surface is preferably 5 μm to 18 μm, more preferably 10 μm to 16 μm. The thickness from the most outer surface of the emulsion surface to the lower end of the emulsion layer which is the nearest to a support is preferably 14 μm or less, and the thickness to the lower end of the emulsion layer which is different in color sensitivity from said emulsion layer and is the nearest to a support in the second place to said emulsion layer is preferably 10 μm or less.

As a method for making a layer of the light-sensitive color material for negative images thinner, there may be mentioned a method by reducing a hydrophilic colloid which is a binder. Since a hydrophilic colloid is added for the purposes of maintaining coupler fine oil drops dissolved in silver halide and a high boiling point solvent, preventing increase of fog due to mechanical stress and preventing color contamination caused by diffusion of an oxidized product of a developing agent between layers, it can be reduced to the extent which does not impair these purposes.

As another method for making a layer thinner, there may be mentioned a method by using a coupler having high color developing property.

As another method for making a layer thinner, there may be mentioned a method by reducing a high boiling point solvent and a method in which an intermediate layer is made thinner by adding a scavenger of an oxidized product of a developing agent to the intermediate layer between layers having different color sensitivities.

The total amount of silver halide contained in the light-sensitive silver halide emulsion contained in all the emulsion layers of the light-sensitive silver halide color photographic material for negative images is preferably 6.5 g/m^2 or less, more preferably 2.5 to 6.0 g/m^2, particularly preferably 3.0 to 5.5 g/m^2, most preferably 3.5 to 5.0 g/m^2.

The swelled film thickness at the time of development of the totally hydrophilic protective colloid layer provided by coating on a support at an emulsion layer side of the light-sensitive silver halide color photographic material for negative images is preferably 180 % to 350 %, particularly preferably 200 % to 300 % of the dried film thickness.

A technique for thus controlling the swelled film thickness is well known in the art, and the thickness can be controlled by selecting, for example, an amount and a kind of a hardener suitably.

As the hardener, there can be used aldehyde and aziridine type hardeners (e.g. those disclosed in PB Report 19,921, U.S. Patents No. 2,950,197, No. 2,964,404, No. 2,983,311 and No. 3,271,175, Japanese Patent Publication No. 40898/1971, and Japanese Unexamined Patent Publication No. 91315/1975), isoxazole type hardeners (e.g. those disclosed in U.S. Patent No. 331,609), epoxy type hardeners (e.g. those disclosed in U.S. Patent No. 3,047,394, West German Patent No. 1,085,663, U.K. Patent No. 1,033,518 and Japanese Patent Publication No. 35495/1973), vinyl sulfone type hardeners (e.g. those disclosed in PB Report 19,920, West German Patents No. 1,100,942, No. 2,337,412, No. 2,545,722, No. 2,635,518, No. 2,742,308 and No. 2,749,260, U.K. Patent No. 1,251,091, Japanese Unexamined Patent Publications No. 150556/1971 and No. 3450/1975, U.S. Patents No. 3,539,644 and No. 3,490,911), acryloyl type hardeners (e.g. those disclosed in Japanese Unexamined Patent Publication No. 154675/1974 and U.S. Patent No. 3,640,720), carbodiimide type hardeners (e.g. those disclosed in U.S. Patents No. 2,938,892, No. 4,043,818 and No. 4,061,499, Japanese Patent Publication No. 38715/1971 and Japanese Unexamined Patent Publication No. 140154/1974), triazine type hardeners (e.g. those disclosed in West German Patents No. 2,410,973 and No. 2,553,915, U.S. Patent No. 3,325,287 and Japanese Unexamined Patent Publication No. 12722/1977), high molecular type hardeners (e.g. those disclosed in U.K. Patent No. 822,061, U.S. Patents No. 3,623,878, No. 3,396,029 and No. 3,226,234, Japanese Patent Publications No. 18578/1972, No. 18579/1972 and No. 48896/1972), and otherwise maleimide type, acetylene type and methanesulfonate type (N-methylol type) hardeners, singly or in combination. As useful combination techniques, there may be mentioned, for example, combinations disclosed in West German Patents No. 2,447, 587, No. 2,505,746 and No. 2,514,245, U.S. Patents No. 4,047,957, No. 3,832,181 and No. 3,840,370, Japanese Unexamined Patent Publications No. 43319/1973, No. 63062/1975 and No. 127329/ 1977 and Japanese Patent Publication No. 32364/1973.

In the present invention, the swelled film thickness at the time of development is defined as a thickness after dipping for 3 minutes in the following solution maintained at 38 °C.

Solution for measuring swelled degree

4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline·sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine·1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Nitrilotriacetic acid·trisodium salt (monohydrate)	2.5 g
Potassium hydroxide	1.0 g

made up 1 liter with addition of water.

The swelled film thickness can be measured according to, for example, a method described in A. Green and G.I.B. Levenson, Journal of Photographic Science, 20, 205 (1972).

The swelled film thickness refers to a film thickness measured at 23 °C and under a controlled humidity of 55 %. Sections of dried samples are enlarged and photographed by a scanning electron microscope, and film thicknesses of the respective layers are measured.

As the above totally hydrophilic protective colloid layer, there may be included in addition to blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers each of which has at least one layer as described above, and further, a protective layer, an antihalation layer, an yellow filter layer and an intermediate layer provided by coating if necessary.

The layer structure of the light-sensitive silver halide color photographic material for negative images which can exhibit the effect according to the present invention particularly is a layer structure comprising a colloidal silver antihalation layer, (an intermediate layer), a red-sensitive layer, (an intermediate layer), a green-sensitive layer, (an intermediate layer), a colloidal silver yellow filter layer, a blue-sensitive layer, (an intermediate layer) and a protective layer coated successively in this order from a support, and further a layer structure comprising a colloidal silver antihalation layer, (an intermediate layer), a red-sensitive layer, (an intermediate layer), a green-sensitive layer, (an intermediate layer), a blue-sensitive layer, (an intermediate layer), a red-sensitive layer, (an intermediate layer), a green-sensitive layer, (a colloidal silver yellow filter layer), a blue-sensitive layer, (an intermediate layer) and a protective layer coated successively in this order from a support.

The layers in the parentheses may be omitted. The respective layers of the above red-sensitive layer, green-sensitive layer and blue-sensitive layer are preferably divided into high sensitivity layers and low sensitivity layers, respectively. Further, there may be included a layer structure in which at least one of a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer is divided into three partial layers as disclosed in Japanese Patent Publication No. 15495/1974, a layer structure in which a high sensitivity emulsion layer unit and a low sensitivity emulsion layer unit are divided as disclosed in Japanese Unexamined Patent Publication No. 49027/1976, and various layer constitutions as disclosed in West German Publications No. 2,622,922, No. 2,622,923, No. 2,622,924, No. 2,704,826 and No. 2,704,797.

In the present invention, layer constitutions disclosed in Japanese Unexamined Patent Publications No. 177551/1982, No. 177552/1984 and No. 180555/1984 can be also applied.

These silver halide emulsions may be chemically sensitized by using active gelatin; sulfur sensitizers such as allylthiocarbamide, thiourea and cystine; selenium sensitizers; reducing sensitizers such as stannous salt, thiourea dioxide and polyamine; noble metal sensitizers such as a gold sensitizer, specifically including potassium aurithiocyanate, potassium chloroaurate and 2-aurothio-3-methylbenzothiazolium chloride, or, for sensitizers of water-soluble groups such as ruthenium, palladium, platinum, rhodium and iridium, specifically including ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladate (some kinds of these act as a sensitizer or a fog restrainer depending on the amount used) singly or in suitable combination (e.g. a combination of a gold sensitizer and a sulfur sensitizer and a combination of a gold sensitizer and a selenium sensitizer).

The silver halide emulsion is chemically ripened by adding a sulfur-containing compound, and prior to this chemical ripening, during ripening or after ripening, at least one hydroxytetrazaindenes and at least one nitrogen-containing heterocyclic compounds having a mercapto group may be contained in the silver halide emulsion.

For imparting a sensitivity to the respective desired light-sensitive wavelength regions, silver halide may be optically sensitized by adding an appropriate sensitizing dye in an amount of 5×10^{-8} to 3×10^{-3} mole per mole of silver halide. As the sensitizing dye, various sensitizing dyes can be used singly or in combination of two or more kinds. As the sensitizing dye advantageously used in the present invention, there may be mentioned, for example, those mentioned below.

Specifically, as a sensitizing dye used in the blue-sensitive silver halide emulsion, there may be mentioned, for example, those disclosed in West German Patent No. 929,080, U.S. Patents No. 2,231,658, No. 2,493,748, No. 2,503,776, No. 2,519,001, No. 2,912,329, No. 3,656,959, No. 3,672,897, No. 3,694,217, No. 4,025,349 and No. 4,046,572, U.K. Patent No. 1,242,588, and Japanese Patent Publications No. 14030/1969 and No. 24844/1977. As a sensitizing dye used in the green-sensitive silver halide emulsion, there may be typically mentioned, for example, cyanine dyes, merocyanine dyes or composite cyanine dyes disclosed in U.S. Patents No. 1,939,201, No. 2,072,908, No. 2,739,149 and No. 2,945,763 and U.K. Patent No. 505,979. Further, as a sensitizing dye used in the red-sensitive silver halide emulsion, there may be typically mentioned, for example, cyanine dyes, merocyanine dyes or composite cyanine dyes disclosed in U.S. Patents No. 2,269,234, No. 2,270,378, No. 2,442,710, No. 2,454,629 and No. 2,776,280. Furthermore, cyanine dyes, merocyanine dyes or composite cyanine dyes disclosed in U.S. Patents No. 2,213,995, No. 2,493,748 and No. 2,519,001 and West German Patent No. 929,080 can be used advantageously in the green-sensitive silver halide emulsion or the red-sensitive silver halide emulsion.

These sensitizing dyes may be used singly or in combination of these.

If necessary, according to a spectral sensitization method by using cyanine or merocyanine dyes singly or in combination, an optical sensitization to a desired wavelength region may be effected.

As a particularly preferred spectral sensitization method, there may be typically mentioned, for example, methods by using a combination of benzimidazolocarbocyanine with benzoxazolocarbocyanine disclosed in Japanese Patent Publications No. 4936/1968, No. 22884/1968, No. 18433/1970, No. 37443/1972, No. 28293/1973, No. 6209/1974 and No. 12375/1978, and Japanese Unexamined Patent Publications No. 23931/1977, No. 51932/1977, No. 80118/1979, No. 153926/1983, No. 116646/1984 and No. 116647/1984.

As a method by using a combination of carbocyanine having a benzimidazole nucleus with another cyanine or merocyanine, there may be mentioned, for example, those disclosed in Japanese Patent Publications No. 25831/1970, No. 11114/1972, No. 25379/1972, No. 38406/1973, No. 38407/1973, No. 34535/1979 and No. 1569/1980, and Japanese Unexamined Patent Publications No. 33220/1975, No. 38526/1975, No. 107127/1976, No. 115820/1976, No. 135528/1976, No. 104916/1977 and No. 104917/1977.

As a method by using a combination of benzoxazolocarbocyanine (oxacarbocyanine) with another carbocyanine, there may be mentioned, for example, those disclosed in Japanese Patent Publications No. 32753/1969 and No. 11627/1971 and Japanese Unexamined Patent Publication No. 1483/1982, and as a method by using merocyanine, there may be mentioned, for example, those disclosed in Japanese Patent Publications No. 38408/1973, No. 41204/1973 and No. 40662/1975 and Japanese Unexamined Patent Publications No. 25728/1981, No. 10753/1983, No. 91445/1983, No. 116645/1984 and No. 33828/1975.

As a method by using a combination of thiacarbocyanine with another carbocyanine, there may be mentioned, for example, those disclosed in Japanese Patent Publications No. 4932/1968, No. 4933/1968, No. 26470/1970, No. 18107/1971, and No. 8741/1972 and Japanese Unexamined Patent Publication No. 114533/1984, and further, a method by using zeromethine or dimethinemerocyanine, monomethine or trimethinecyanine and a styryl dye disclosed in Japanese Patent Publication No. 6207/1974 can be used advantageously.

These sensitizing dyes are previously dissolved in a hydrophilic organic solvent, for example, methyl alcohol, ethyl alcohol, acetone, dimethylformamide or fluorinated alcohol disclosed in Japanese Patent Publication No. 40659/1975, and added in the form of a dye solution.

The time of addition may be any desired period such as the time of initiating the chemical ripening of the silver halide emulsion, during the ripening and the time of completion of the ripening, and may be at the step immediately before emulsion coating depending on the case.

In the photographic constituent layer of the light-sensitive silver halide color photographic material, a dye which is water-soluble or decolored by a color developing solution (AI dye) can be added, and said AI dye may include oxonol dyes, hemioxonol dyes, merocyanine dyes and azo dyes. Among them, oxonol dyes, hemioxonol dyes and merocyanine dyes are useful. As an example of the AI dye which can be used, there may be mentioned those disclosed in U.K. Patents No. 584,609 and No. 1,277,429, Japanese Unexamined Patent Publications No. 85130/1973, No. 99620/1974, No. 114420/1974, No. 129537/1974, No. 108115/1977, No. 25845/1984, No. 111640/1984 and No. 111641/1984, U.S. Patents No. 2,274,782, No. 2,533,472, No. 2,956,079, No. 3,125,448, No. 3,148,187, No. 3,177,078, No. 3,247,127, No. 3,260,601, No. 3,540,887, No. 3,575,704, No. 3,653,905, No. 3,718,472 and No. 4,070,352.

These AI dyes are generally used preferably in an amount of 2×10^{-3} to 5×10^{-1} mole per mole of silver in the emulsion layer.

Further, in addition to a DIR compound, a compound releasing a development inhibitor in accompaniment with development can be also used in the present invention, and may include, for example, those disclosed in U.S. Patents No. 3,297,445 and No. 3,379,529, West German Patent Application (OLS) No. 2,417,914, and Japanese Unexamined Patent Publications No. 15271/1977, No. 9116/1978, No. 123838/1984 and No. 127038/1984.

The DIR compound is a compound which can release a development inhibitor by reaction with an oxidized product of a color developing agent.

A representative example of such a DIR compound is a DIR coupler in which a group capable of forming a compound having development inhibition action when eliminated from an active site of the coupler is introduced to an active site of the coupler, and disclosed in, for example, U.K. Patent No. 935,454, U.S. Patents No. 3,227,554, No. 4,095,984 and No. 4,149,886.

When the above DIR coupler undergoes coupling reaction with an oxidized product of a color developing agent, a coupler mother nucleus forms a dye, and on the other hand, it has property of releasing a development inhibitor. Further, in the present invention, there may be included compounds which release a development inhibitor, but not form a dye by coupling reaction with an oxidized product of a color developing agent, as disclosed in U.S. Patents No. 3,652,345, No. 3,928,041, No. 3,958,993, No. 3,961,959 and No. 4,052,213, and Japanese Unexamined Patent Publications No. 110529/1978, No. 13333/1979 and No. 161237/1980.

Furthermore, a compound in which a mother nucleus forms a dye or a colorless compound when reacted with an oxidized product of a color developing agent, and on the other hand, a timing group eliminated releases a development inhibitor by the intermolecular nucleophilic substitution reaction or elimination reaction as disclosed in Japanese Unexamined Patent Publications No. 145135/1979, No. 114946/1981 and No. 154234/1982, a so-called timing DIR compound can be also used in the present invention.

Also, timing DIR compounds in which the timing group as described above is bonded to a coupler mother nucleus which forms a totally diffusible dye when reacted with an oxidized product of a color developing agent disclosed in Japanese Unexamined Patent Publications No. 160954/1983 and No. 162949/1983 can be also used.

The amount of the DIR compound to be contained in the light-sensitive material is preferably in the range of 1×10^{-4} mole to 10×10^{-1} mole per mole of silver.

The silver halide grains to be used in the case of the light-sensitive color material for positive images (e.g. a color negative paper) have a silver chloride content of 90 mole % or more, a silver bromide content of 10 mole % or less and a silver iodide content of 0.5 mole % or less, and more preferably, the silver halide grains are silver chlorobromide having a silver bromide content of 0.1 to 2 mole %.

Said silver halide grains may be used alone or in combination with other silver halide grains having different compositions, and further may be used in combination with silver halide grains having a silver chloride content of 10 mole % or less.

In the silver halide emulsion layer containing the silver halide grains having a silver chloride content of 90 mole % or more, the rate of the silver halide grains having a silver chloride content of 90 mole % or more in all the silver halide grains contained in said emulsion layer is 60 % by weight or more, preferably 80 % by weight or more.

The above silver halide grains may comprise a uniform composition from an inner portion to an outer portion of the grain, or different compositions between an inner portion and an outer portion of the grain. When compositions are different between an inner portion and an outer portion, the compositions may change continuously or discontinuously.

The grain size of the above silver halide grains is not particularly limited, but may be 0.2 to 1.6 μm, more preferably in the range of 0.25 to 1.2 μm in consideration of rapid processing characteristics and other photographic performances such as sensitivity.

The above grain size can be measured according to various methods generally used in this technical field. The representative method is described in "Grain Size Analysis Method" (A.S.T.M. Symposium on Light Microscopy, 1955, pp. 94 to 122) by Labland or "Theory of Photographic Process" (written by Meeth and James, 3rd edition, Chapter 2, published by McMillan Co. (1966)).

The grain size can be measured by using projected area or an approximate diameter value of the grain. When the grains have a substantially uniform shape, its grain side distribution can be represented fairly precisely as a diameter or projected area.

The grain size distribution of the above silver halide grains may be polydispersed or monodispersed. Preferred is a monodispersed silver halide grain having a coefficient of variation of 0.22 or less, more preferably 0.15 or less in the grain size distribution of the silver halide grains. Here, the coefficient of variation is a coefficient showing a width of a grain size distribution, and defined by the following formula.

$$\text{Variation coefficient } (S/\bar{r}) = \frac{\text{Standard deviation of grain size distribution}}{\text{Average grain size}}$$

$$\text{Standard deviation of grain size distribution } (S) = \sqrt{\frac{\Sigma(\bar{r}-ri)^2 ni}{\Sigma ni}}$$

$$\text{Average grain size } (\bar{r}) = \sqrt{\frac{\Sigma niri}{\Sigma ni}}$$

Here, ri represents a grain size of each grain, and ni represents a number of grains. When the silver halide grain is spherical, the grain size mentioned here represents its diameter, and when the silver halide grain has a shape other than cube or sphere, it represents a diameter obtained by converting its projected area to a circle area having the same area.

The silver halide grains to be used in the above emulsion may be obtained according to any method such as an acidic method, a neutral method and an ammoniacal method. Said grains may be grown at one time or may be grown after seed grains are formed. A method for forming seed grains and a method for growing them may be the same or different.

The system for reacting soluble silver salts with soluble halogen salts may be a normal precipitation, a reverse precipitation, a simultaneous precipitation or a mixture thereof, but preferably a simultaneous precipitation. As one system of the simultaneous precipitation, a pAg controlled double jet method disclosed in Japanese Unexamined Patent Publication No. 48521/1979 can be also used.

Further, if necessary, a silver halide solvent such as thioether may be used. Also, a mercapto group-containing compound, a nitrogen-containing heterocyclic compound or a compound such as a sensitizing dye may be added at the time of forming the silver halide grains or after completion of forming the grains.

The above silver halide grains can have any desired shape. One preferred example is a cube having {100} phase as a crystalline surface. There may be also employed grains having a shape of octahedron, tetradecahedron or dodecahedron prepared according to the methods disclosed in U.S. Patents No. 4,183,756 and No. 4,225,666, Japanese Unexamined Patent Publication No. 226589/1980, Japanese Patent Publication No. 42737/1980 and The Journal of Photographic Science, 21, 39 (1973). Further, grains having a twin surface may be also used. The silver halide grains according to the present invention may be grains comprising a single shape or a mixture of grains having various shapes.

In the above silver halide grains, in the step of forming the grains and/or the step of growing the grains, a metal ion such as a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof and an iron salt or a complex salt thereof can be added to be contained internally of the grain and/or on a grain surface. By placing the grains under an appropriate reducing atmosphere, a reducing sensitizing nucleus can be given internally of the grain and/or a grain surface.

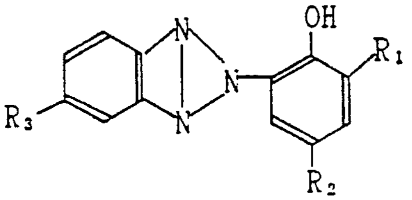
After completion of growing of the silver halide grains, unnecessary soluble salts may be removed from the emulsion containing the above silver halide grains, or may be contained therein. Said salts can be removed according to a method described in Research Disclosure No. 17643.

The above silver halide grains may be a grain of which a latent image is mainly formed on a grain surface or a grain of which a latent image is mainly formed internally of a grain, but preferably a grain of which a latent image is mainly formed on a grain surface.

The above emulsion can be chemically sensitized according to a conventional method.

The respective silver halide emulsions of the light-sensitive color photographic material for positive images are preferably arranged from a support side in the order of a blue-sensitive silver halide emulsion layer containing a yellow coupler, a green-sensitive silver halide emulsion layer containing a magenta coupler and a red-sensitive silver halide emulsion layer containing a cyan coupler, and in the whole light-sensitive material, it is preferred that a blue-sensitive silver halide emulsion layer containing a yellow coupler, a green-sensitive silver halide emulsion layer containing a magenta coupler, a non-light-sensitive intermediate layer containing a UV absorber, a red-sensitive silver halide emulsion layer containing a cyan coupler, a non-light-sensitive layer containing a UV absorber and a protective layer are arranged on a support as essential layers in this order from said support side.

As the UV absorber, those represented by the following formula (U) are preferred.



(U)

wherein R_1, R_2 and R_3 each represent a hydrogen atom, a halogen atom, an alkyl gorup, an aryl group, an alkoxy group, an aryloxy group, an alkenyl group, a nitro group and a hydroxyl group.

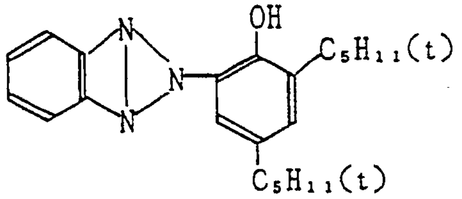
The respective groups represented by R_1 to R_3 include those having a substituent group.

Among the groups represented by R_1 and R_2, a hydrogen atom, an alkyl group, an alkoxy group and an aryl group are preferred, and particularly, a hydrogen atom, an alkyl group and an alkoxy group are preferred.

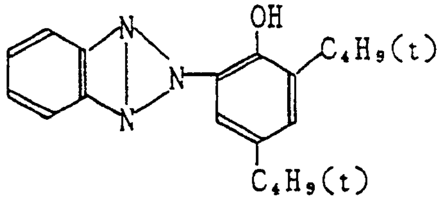
Among the groups represented by R_3, a hydrogen atom, a halogen atom, an alkyl group and an alkoxy group are particularly preferred.

At least one of R_1 to R_3 is preferably an alkyl group, and further, at least two of them are preferably alkyl groups. At least one of R_1 to R_3 is preferably a branched alkyl group.

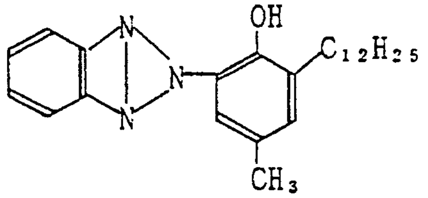
Representative specific examples are shown below.



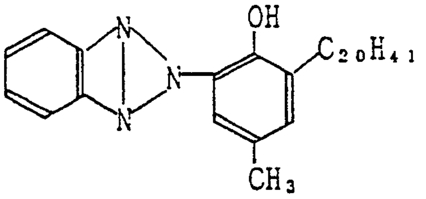
(U-1)



(U-2)



(U-3)



(U-4)

The amount to be added of the compound represented by the formula (U) is preferably 0.1 to 300 % by weight, more preferably 1 to 200 % by weight based on a binder in the layer to which said compound is added.

In the light-sensitive silver halide color photographic material to be used in the present invention, various additives for photography can be further contained. There can be used, for example, an antifoggant, a stabilizer, a UV absorber, a color antistaining agent, a fluorescent brightener, a color image anti-fading agent, an antistatic agent, a hardener, a surfactant, a plasticizer and a lubricant described in Research Disclosure No. 17643.

In the light-sensitive silver halide color photographic material to be used in the present invention, a hydrophilic colloid to be used for preparing the emulsion may include any desired one such as gelatin, gelatin derivatives, graft polymers of gelatin and other polymers, proteins such as albumin and casein, cellulose derivatives such as hydroxyethyl cellulose derivatives and carboxymethyl cellulose derivatives, starch derivatives and synthetic hydrophilic polymers of homopolymers or copolymers such as polyvinyl alcohol, polyvinylimidazole and polyacrylamide.

As a support of the light-sensitive silver halide color photographic material to be used in the present invention, there may be mentioned, for example, a baryta paper, a polyethylene-coated paper, a polypropylene synthetic paper, a transparent support provided with a reflective layer or used in combination with a reflector, for example, a glass plate, polyester films such as cellulose acetate, cellulose nitrate or polyethylene terephthalate, a polyamide film, a polycarbonate film and a polystyrene film, and also other transparent supports used in general.

These supports are selected suitably depending on the use of the light-sensitive material.

EXAMPLES

The present invention is described in detail below by referring to Examples, but the present invention is not limited by these Examples at all.

Example 1

In all Examples, the amount added in the light-sensitive silver halide photographic material is represented in a number of grams per 1 m^2 unless otherwise indicated, and the amounts of silver halide and colloidal silver are represented by calculating them on silver.

On a triacetyl cellulose film support, the respective layers having the compositions shown below were formed successively from a support side to prepare Sample I of a multilayer color photographic element.

Sample I

First layer: Antihalation layer (HC-1)	
Black colloidal silver	0.20
UV absorber (UV-1)	0.20
Colored coupler (CC-1)	0.05
Colored coupler (CM-2)	0.06
High boiling point solvent (Oil-1)	0.20
Gelatin	1.5
Second layer: Intermediate layer (IL-1)	
UV absorber (UV-1)	0.01
High boiling point solvent (Oil-1)	0.01
Gelatin	1.3
Third layer: Low sensitivity red-sensitive emulsion layer (RL)	

Silver iodobromide emulsion (Em-1)	1.0
Silver iodobromide emulsion (Em-2)	0.7
Sensitizing dye (S-1)	2.2×10^{-4} (mole/mole of silver)
Sensitizing dye (S-2)	2.5×10^{-4} (mole/mole of silver)
Sensitizing dye (S-3)	0.5×10^{-4} (mole/mole of silver)
Cyan coupler (C'-4)	1.3
Cyan coupler (C'-2)	0.15
Colored cyan coupler (CC-1)	0.05
DIR compound (D-1)	0.0015
High boiling point solvent (Oil-1)	0.5
Gelatin	1.3

Fourth layer: High sensitivity red-sensitive emulsion layer (RH)

Silver iodobromide emulsion (Em-3)	2.2
Sensitizing dye (S-1)	2.2×10^{-4} (mole/mole of silver)
Sensitizing dye (S-2)	2.0×10^{-4} (mole/mole of silver)
Sensitizing dye (S-3)	0.1×10^{-4} (mole/mole of silver)
Cyan coupler (C'-1)	0.15
Cyan coupler (C'-2)	0.018
Cyan coupler (C'-3)	1.20
Colored cyan coupler (CC-1)	0.015
DIR compound (D-2)	0.04
High boiling point solvent (Oil-1)	0.5
Gelatin	1.3

Fifth layer: Intermediate layer (IL-2)

Gelatin	0.5

Sixth layer: Low sensitivity green-sensitive emulsion layer (GL)

Silver iodobromide emulsion (Em-1)	0.9
Sensitizing dye (S-4)	5×10^{-4} (mole/mole of silver)

Sensitizing dye (S-5)	1×10^{-4} (mole/mole of silver)
Magenta coupler (M'-1)	0.5
Colored magenta coupler (CM-1)	0.05
DIR compound (D-3)	0.015
DIR compound (D-4)	0.020
High boiling point solvent (Oil-2)	0.5
Gelatin	1.2
Seventh layer: Intermediate layer (IL-3)	
Gelatin	0.7
High boiling point solvent (Oil-1)	0.2
Eighth layer: High sensitivity green-sensitive emulsion layer (GH)	
Silver iodobromide emulsion (Em-3)	1.2
Sensitizing dye (S-6)	1.5×10^{-4} (mole/mole of silver)
Sensitizing dye (S-7)	2.5×10^{-4} (mole/mole of silver)
Sensitizing dye (S-8)	0.7×10^{-4} (mole/mole of silver)
Magenta coupler (M'-2)	0.08
Magenta coupler (M'-3)	0.18
Colored magenta coupler (CM-2)	0.05
DIR compound (D-3)	0.01
High boiling point solvent (Oil-3)	0.5
Gelatin	1.15
Ninth layer: Yellow filter layer (YC)	
Yellow colloidal silver	0.10
Color antistaining agent (SC-1)	0.1
High boiling point solvent (Oil-3)	0.1
Gelatin	0.9
Tenth layer: Low sensitivity blue-sensitive emulsion layer (BL)	
Silver iodobromide emulsion (Em-1)	0.23
Silver iodobromide emulsion (Em-2)	0.27
Sensitizing dye (S-10)	7.0×10^{-4} (mole/mole of silver)

Yellow coupler (YB-15)	0.6
Yellow coupler (Y-2)	0.12
DIR compound (D-2)	0.01
High boiling point solvent (Oil-3)	0.15
Gelatin	1.0

Eleventh layer: High sensitivity blue-sensitive emulsion layer (BH)

Silver iodobromide emulsion (Em-4)	0.45
Silver iodobromide emulsion (Em-1)	0.22
Sensitizing dye (S-9)	1.3×10^{-4} (mole/mole of silver)
Sensitizing dye (S-10)	3.0×10^{-4} (mole/mole of silver)
Yellow coupler (YB-15)	0.36
Yellow coupler (Y-2)	0.09
High boiling point solvent (Oil-3)	0.07
Gelatin	1.1

Twelfth layer: First protective layer (PRO-1)

Fine silver iodobromide emulsion (average grain size: 0.06 μm, AgI: 2.0 mole %)	0.25
UV absorber (UV-1)	0.10
UV absorber (UV-2)	0.05
High boiling point solvent (Oil-1)	0.1
High boiling point solvent (Oil-4)	0.1
Formalin scavenger (HS-1)	0.5
Formalin scavenger (HS-2)	0.2
Gelatin	1.0

Thirteenth layer: Second protective layer (PRO-2)

Surfactant (Su-1)	0.005
Alkali-soluble matting agent (average grain size: 2 μm)	0.10
Cyan dye (AIC-1)	0.005
Magenta dye (AIM-1)	0.01
Slipping agent (WAX-1)	0.04
Gelatin	0.6

In the respective layers, in addition to the compositions as described above, a coating aid Su-2, a dispersing aid Su-3, an antiseptic agent DI-1, a stabilizer Stab-1, and antifoggants AF-1 and AF-2 were added.

Em-1

Monodispersed emulsion in which a small amount of silver iodide is contained in the surface, having an average grain size of 0.45 μm and an average silver iodide content of 7.5 mole %.

Em-2

Monodispersed emulsion of which the composition is uniform, having an average grain size of 0.30 μm and an average silver iodide content of 2.1 mole %.

Em-3

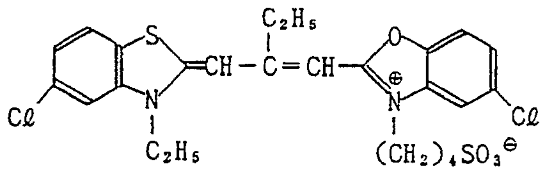
Monodispersed emulsion in which a small amount of silver iodide is contained in the surface, having an average grain size of 0.81 μm and an average silver iodide content of 6.1 mole %.

Em-4

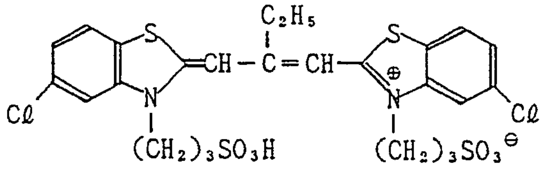
Monodispersed emulsion in which a small amount of silver iodide is contained in the surface, having an average grain size of 0.98 μm and an average silver iodide content of 8.0 mole %.

Em-1, Em-3 and Em-4 are silver iodobromide emulsions mainly comprising octahedrons and having a multilayer structure prepared by referring to Japanese Unexamined Patent Publications No. 138538/1985 and No. 245151/1986. Em-1 to Em-4 each had an average value of grain size/grain thickness of 1.0 and had a grain distribution width of 12, 8, 12 and 10 %, respectively.

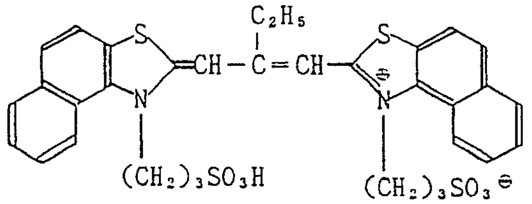
S - 1



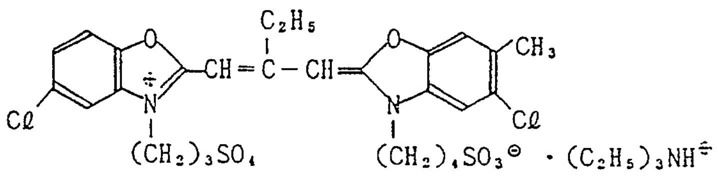
S - 2



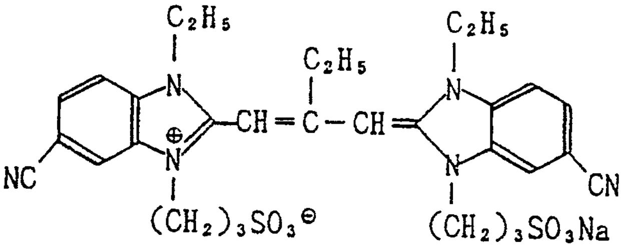
S - 3



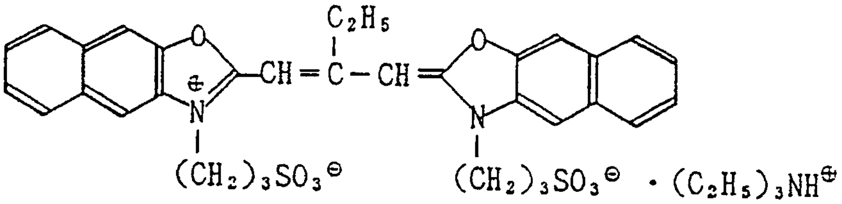
S - 4



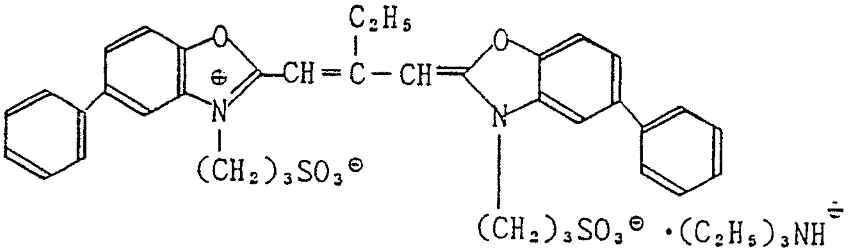
S - 5


C2H5
C2H5
C2H5
N
N
N
N
CH = C - CH
NC
CN
(CH2)3SO3⊖
(CH2)3SO3Na

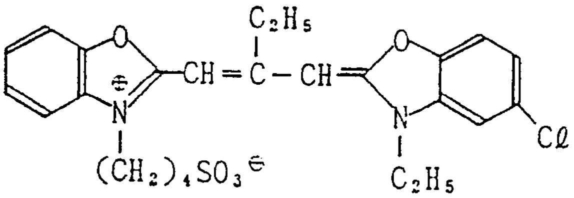
S - 6


C2H5
O
O
CH = C - CH
N
N
(CH2)3SO3⊖
(CH2)3SO3⊖ · (C2H5)3NH⊕

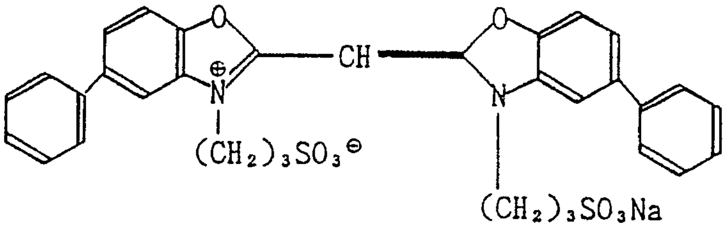
S - 7


C2H5
O
O
CH = C - CH
N
N
(CH2)3SO3⊖
(CH2)3SO3⊖ ·(C2H5)3NH⊕

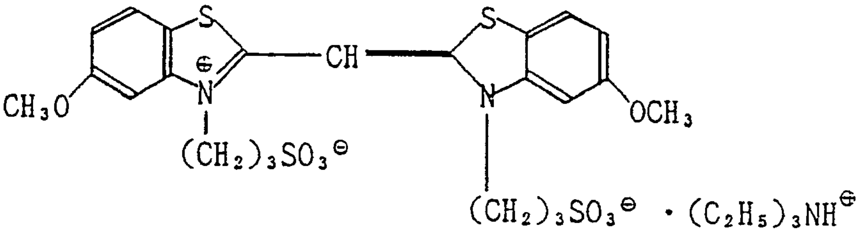
S - 8


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

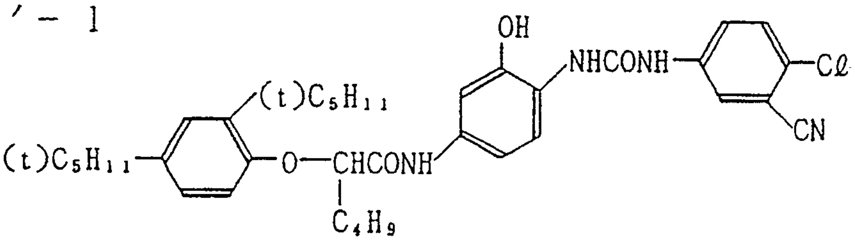
S - 9


O
CH
O
N
N
$(CH_2)_3SO_3^{\ominus}$
$(CH_2)_3SO_3Na$

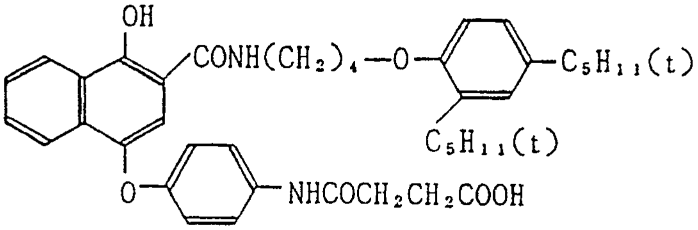
S - 10


S
CH
S
CH_3O
N
N
OCH_3
$(CH_2)_3SO_3^{\ominus}$
$(CH_2)_3SO_3^{\ominus}\cdot(C_2H_5)_3NH^{\oplus}$

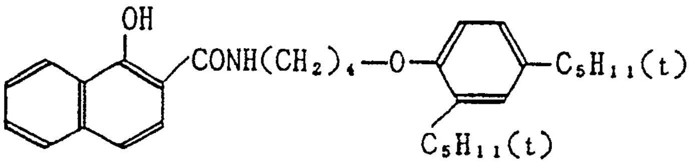
C′ - 1


OH
NHCONH
Cl
$(t)C_5H_{11}$
$(t)C_5H_{11}$
O
CHCONH
CN
C_4H_9

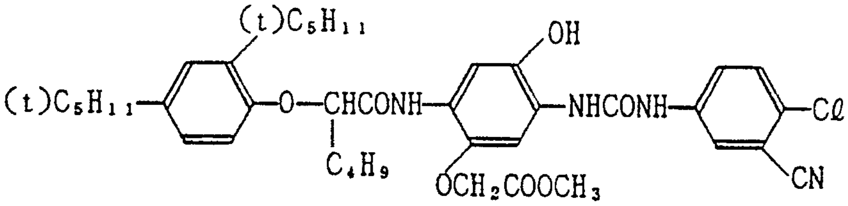
C′ - 2


OH
$CONH(CH_2)_4$
O
$C_5H_{11}(t)$
$C_5H_{11}(t)$
O
$NHCOCH_2CH_2COOH$

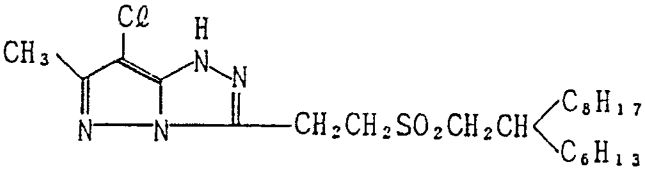
C′-3



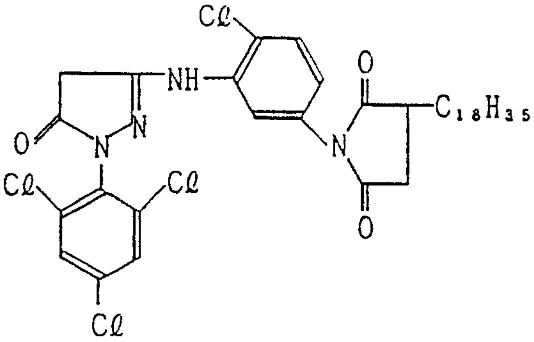
C′-4



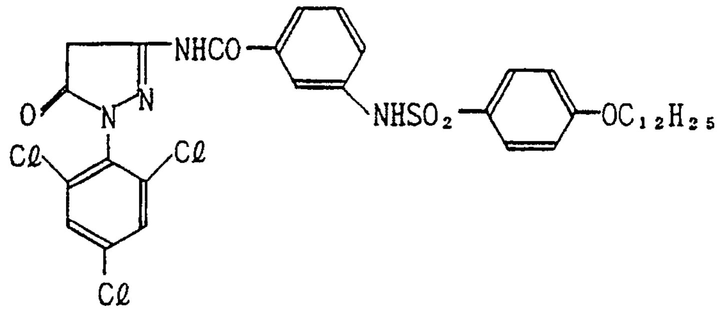
M′-1



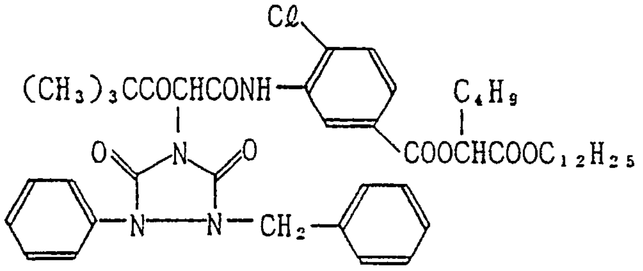
M′-2



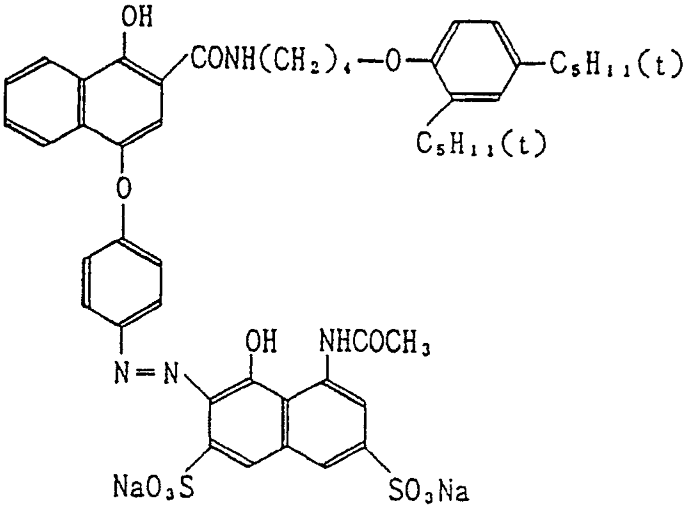
M′ − 3


NHCO
NHSO₂
OC₁₂H₂₅
O
N
N
Cℓ
Cℓ
Cℓ

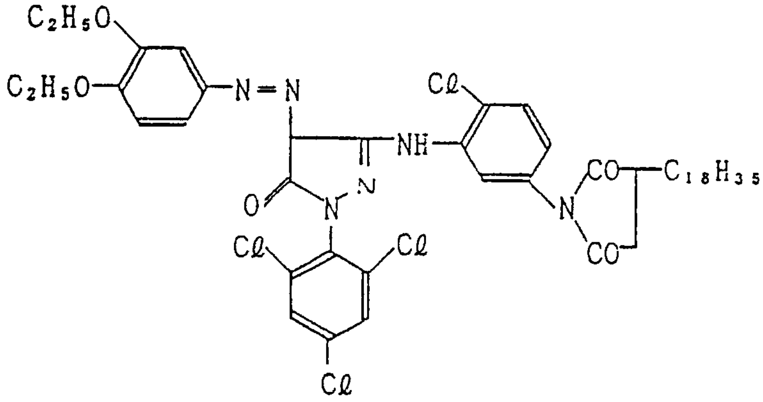
Y − 2


Cℓ
(CH₃)₃CCOCHCONH
C₄H₉
COOCHCOOC₁₂H₂₅
O
N
O
N
N
CH₂

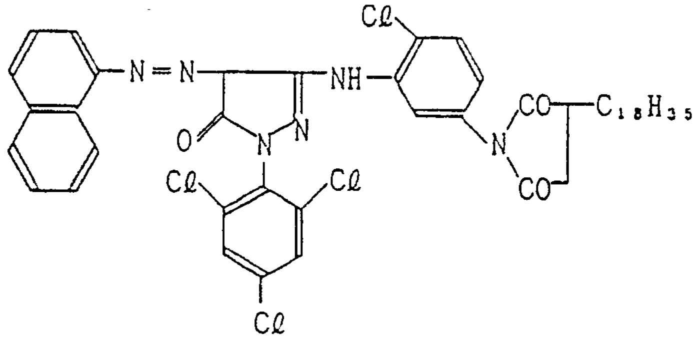
CC－1



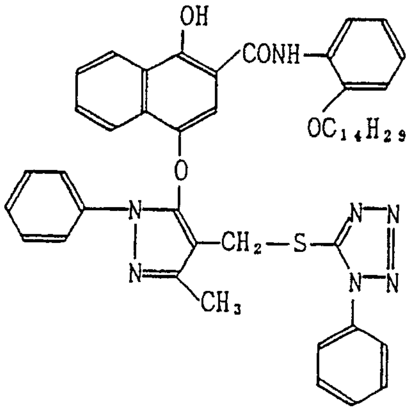
CM－1



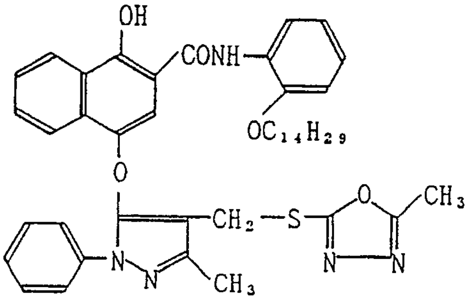
CM－2



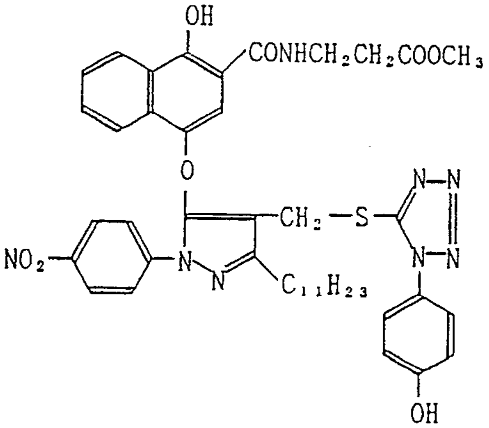
D − 1


OH
CONH
OC₁₄H₂₉
O
N
N
CH₂—S
N—N
N—N
CH₃

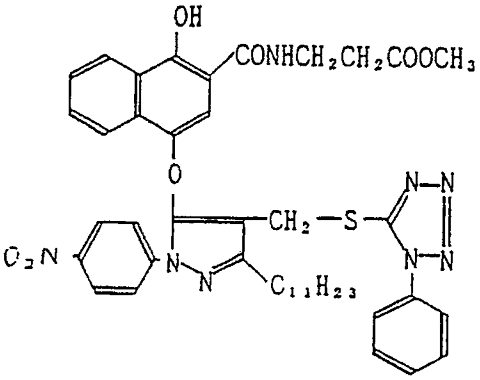
D − 2


OH
CONH
OC₁₄H₂₉
O
CH₂—S
O
CH₃
N
N
N
N
CH₃

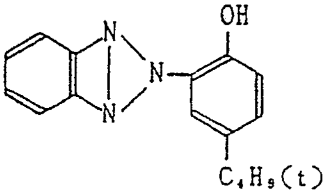
D − 3


OH
CONHCH₂CH₂COOCH₃
O
CH₂—S
N—N
N—N
NO₂
N
N
C₁₁H₂₃
OH

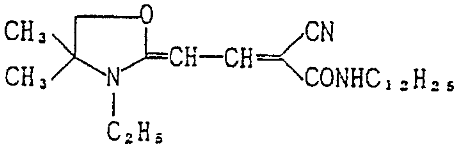
D－4



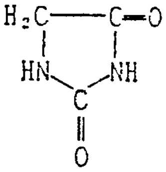
UV－1



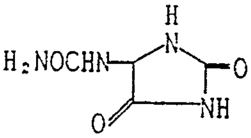
UV－2



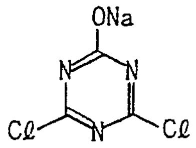
HS－1



HS－2



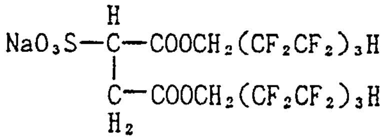
H－1



H－2

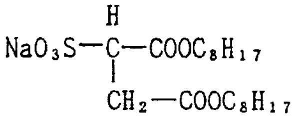
$[(CH_2=CHSO_2CH_2)_3CCH_2SO_2(CH_2)_2]_2N(CH_2)_2SO_3K$

Su－1



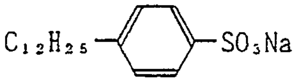
$$\begin{array}{l} \quad\quad\quad\;\; H \\ NaO_3S-C-COOCH_2(CF_2CF_2)_3H \\ \quad\quad\quad\;\; | \\ \quad\quad\quad\;\; C-COOCH_2(CF_2CF_2)_3H \\ \quad\quad\quad\;\; H_2 \end{array}$$

Su－2

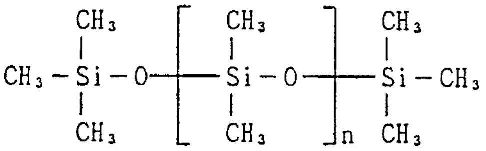


$$\begin{array}{l} \quad\quad\quad\;\; H \\ NaO_3S-C-COOC_8H_{17} \\ \quad\quad\quad\;\; | \\ \quad\quad\quad\;\; CH_2-COOC_8H_{17} \end{array}$$

Su－3

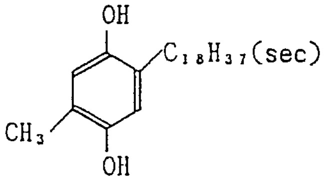


WAX－1

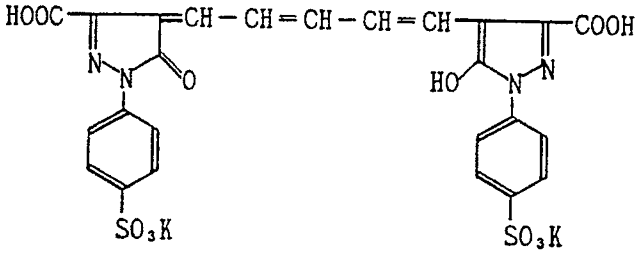


$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

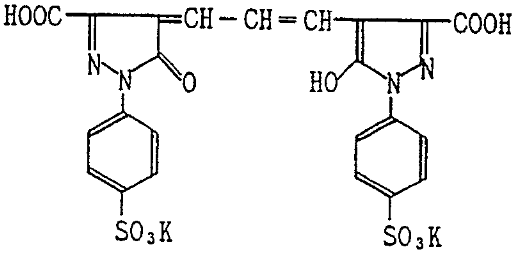
Sc－1



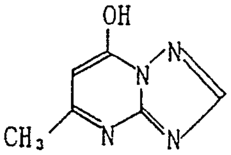
AIC-1



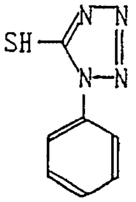
AIM-1



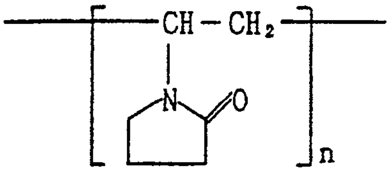
Stab-1



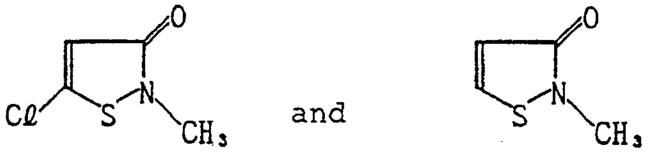
AF-1



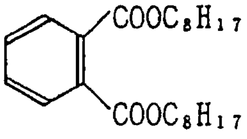
AF－2



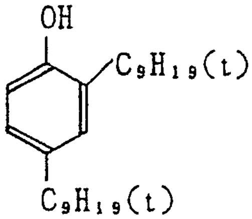
DI－1



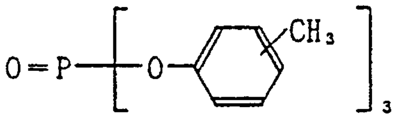
Oil－1



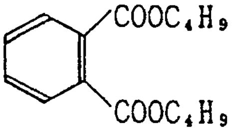
Oil－2



Oil－3



Oil－4



The samples thus prepared were subjected to wedge exposure by using white lights, and then the following development processings were carried out.

(Processings for experiment)

Processing step	Processing time	Processing temperature
Color development (one tank)	3 min 15 sec	38 °C
Bleaching (one tank)	35 sec	38 °C
Fixing (one tank)	1 min 10 sec	38 °C
Stabilizing (3 tank cascade)	1 min	38 °C
Drying (40 °C to 80 °C)	1 min	

The color developing solution used had the following composition.

Potassium carbonate	30 g
Sodium hydrogen carbonate	2.5 g
Potassium sulfite	3.0 g
Sodium bromide	1.3 g
Potassium iodide	1.2 mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)aniline sulfate	4.5 g
Diethylenetriaminepentaacetic acid	3.0 g
Potassium hydroxide	1.2 g

made up to 1 liter with addition of water, and adjusted pH to 10.06 with potassium hydroxide or 20 % sulfuric acid.

The bleaching solution used had the following composition.

Ferric organic acid sodium salt	(shown in Table 1)
Disodium ethylenediaminetetraacetate	10 g
Potassium bromide	150 g
Glacial acetic acid	40 ml

Color developing solution shown above 250 ml made up to 1 liter with addition of water, adjusted pH suitably as shown in Table 1 with diethanolamine, aqueous ammonia or glacial acetic acid, and made a rate of an ammonium salt in total cations 5 %.

The fixing solution used had the following composition.

Ammonium thiosulfate	250 g
Anhydrous sodium bisulfite	12 g
Sodium metabisulfite	2.5 g
Disodium ethylenediaminetetraacetate	0.5 g
Bleaching solution shown above	100 ml

made up to 1 liter with addition of water, and adjusted pH to 6.5 with acetic acid and aqueous ammonia.

The stabilizing solution used had the following composition.

Formaldehyde (37 % solution)	0.5 ml
5-Chloro-2-methyl-4-isothiazolin-3-one	0.05 g
Emulgen 810 (trade name)	1 ml
Hexahydro-1,3,5-tris-(2-hydroxyethyl)-5-triazine	0.3 g
Formaldehyde sodium bisulfite adduct	2 g
Hexamethylenetetramine	0.2 g

made up to 1 liter with addition of water, and adjusted pH to 7.0 with aqueous ammonia and 50 % sulfuric acid.

The bleaching solutions prepared by changing a ferric organic acid complex salt, and an amount and a pH thereof as shown in the following Table 1 were stored at 38 °C for one week. After development processings were carried out, yellow transmission densities at unexposed portions of the film samples after processing were measured, and at the same time, amounts of residual silver at exposed portions by irradiation were measured according to the X-ray fluorescence method. Further, tar generation was examined by observing external appearances of the bleaching solutions after storage. The above results are shown together in Table 1.

Table 1

Exper-iment No.	Ferric organic acid complex salt	Amount added (mole/ℓ)	pH	Yellow density at unexposed portion	Amount of residual silver at exposed portion by irradiation (mg/100 cm^2)	Tar generation
1-1	EDTA·Fe	0.30	4.5	0.62	9.6	○
1-2	NTA·Fe	0.30	4.5	0.61	10.1	○
1-3	CyDTA·Fe	0.30	4.5	0.61	9.2	○
1-4	EDTMP·Fe	0.30	4.5	0.62	8.5	○
1-5	NTMP·Fe	0.30	4.5	0.62	9.3	○
1-6	(A-1)·Fe	0.30	4.5	0.63	0.3	○
1-7	(A-4)·Fe	0.30	4.5	0.63	0.4	○
1-8	(A-7)·Fe	0.30	4.5	0.64	0.4	○
1-9	(A-9)·Fe	0.30	4.5	0.61	0.3	○
1-10	(A-1)·Fe	0.05	4.5	0.60	3.5	○
1-11	(A-1)·Fe	0.10	4.5	0.63	1.0	○
1-12	(A-1)·Fe	0.19	4.5	0.63	0.7	○
1-13	(A-1)·Fe	0.23	4.5	0.63	0.4	○
1-14	(A-1)·Fe	0.40	4.5	0.64	0.2	○

Table 1 (Cont'd)

Experiment No.	Ferric organic acid complex salt	Amount added (mole/ℓ)	pH	Yellow density at unexposed portion	Amount of residual silver at exposed portion by irradiation (mg/100 cm^2)	Tar generation
1-15	(A-1)·Fe	0.50	4.5	0.64	0.2	O
1-16	(A-1)·Fe	0.60	4.5	0.66	0.1	Δ
1-17	(A-1)·Fe	0.30	1.5	0.60	2.2	Δ
1-18	(A-1)·Fe	0.30	2.0	0.60	0.7	Δ
1-19	(A-1)·Fe	0.30	3.0	0.60	0.4	O
1-20	(A-1)·Fe	0.30	4.0	0.61	0.2	O
1-21	(A-1)·Fe	0.30	5.0	0.61	0.3	O
1-22	(A-1)·Fe	0.30	5.5	0.63	0.7	Δ
1-23	(A-1)·Fe	0.30	6.0	0.67	2.2	X
1-24	(A-1)·Fe	0.30	7.0	0.78	4.7	XX

In Table 1, EDTA•Fe means a ferric sodium salt of ethylenediaminetetraacetic acid, NTA•Fe a ferric sodium salt of nitrilotriacetic acid, CyDTA•Fe a ferric sodium salt of 1,2-cyclohexanediaminetetraacetic acid, EDTMP•Fe a ferric sodium salt of ethylenediaminetetramethylene-phosphonic acid, NTMP•Fe a ferric sodium salt of nitrilotrimethylenephosphonic acid, and (A-1)•Fe a ferric sodium salt of (A-1). Similarly, (A-4)•Fe, (A-7)•Fe and (A-9)•Fe mean ferric sodium salts of (A-4), (A-7) and (A-9), respectively.

Further, in Table 1, 0 means no tar generation, Δ slight tar generation and X tar generation apparently recognized, and as a number of X is larger, the extent is larger.

From Table 1 shown above, it can be understood that when a ferric organic acid complex salt is the ferric complex salt of the compound represented by the above formula (A) of the present invention, its amount added is 0.10 mole/ℓ or more, and its pH is 2.0 to 5.5, the yellow fog density at unexposed portions is low, the amount of residual silver is minute, and no tar is generated in the bleaching solution, namely all performances are good. However, when even one of the above three conditions is not satisfied, any of the performances is inferior, whereby the samples cannot be provided for practical use.

Example 2

The rates of ammonium salts in total cations of Experiments No. 1-1, No. 1-6 and No. 1-8 in Example 1 were changed as shown in Table 2, and the same evaluation as in Example 1 was made.

However, the rates of ammonium salt were adjusted by changing rates of an ammonium salt and a sodium salt of ferric complex salts and by adding aqueous ammonia.

The results are shown in Table 2.

Table 2

Experiment No.	Bleaching solution No. (Experiment No. of Example 1)	Rate of ammonium salt in total cations (mole %)	Yellow density of unexposed portion	Amount of residual silver (mg/100cm^2)
2-1	1-1	80	0.65	8.1
2-2	1-1	60	0.64	8.4
2-3	1-1	50	0.63	8.6
2-4	1-1	20	0.62	9.0
2-5	1-1	0	0.62	10.2
2-6	1-6	80	0.73	0.2
2-7	1-6	60	0.68	0.3
2-8	1-6	50	0.65	0.3
2-9	1-6	20	0.63	0.3
2-10	1-6	0	0.63	0.3
2-11	1-8	80	0.72	0.2
2-12	1-8	60	0.68	0.3
2-13	1-8	50	0.65	0.3
2-14	1-8	20	0.64	0.4
2-15	1-8	0	0.64	0.4

As clearly shown in Table 2, when the rate of an ammonium salt in total cations is high, in the ferric complex salt of the present invention, remarkable increase in yellow stain is recognized as compared with EDTA•Fe. Particularly when the rate is 60 % or more, yellow stain becomes high. Further, it can be understood that when the rate of an ammonium salt is high, desilvering property becomes relatively good, but in the case of the ferric complex salt of the present invention, improvement in desilvering property is not so significant.

Example 3

The same light-sensitive silver halide color photographic material used in Example 1 except for changing the silver iodobromide emulsions (Em-1 to 4 and the fine silver iodobromide emulsion) in the third, fourth, sixth, eighth, tenth, eleventh and twelfth layers to silver chlorobromide emulsions shown in the following table were used and processed by using the following processing steps and processing solutions, followed by the same evaluation as in Example 2.

Emulsion	Silver halide composition	Grain size (μ)	Shape of grain
Em-1 -> Em-5	AgBrCl Cl content: 95	0.46	cube
Em-2 -> Em-6	AgBrCl Cl content: 95	0.30	cube
Em-3 -> Em-7	AgBrCl Cl content: 95	0.80	cube
Em-4 -> Em-8	AgBrCl Cl content: 99	0.95	cube
Fine silver halide	AgBrCl Cl content: 99	0.06	octahedron

The above emulsions were prepared by referring to Japanese Unexamined Patent Publications No. 26838/1989 and No. 26837/1989.

<Processing step>	<Processing time>	<Processing temperature>
Color Development	60 sec	38 °C
Bleaching	45 sec	38 °C
Fixing	45 sec	38 °C
Stabilizing (3 tank cascade)	60 sec	38 °C
Drying (40 °C to 80 °C)	60 sec	

The color developing solution used had the following composition.

Triethanolamine	10 g
Ethylene glycol	1 g

N,N-diethylhydroxylamine	3.6 g
Hydrazinodiacetic acid	5.0 g
Potassium bromide	20 mg
Potassium chloride	2.5 g
Diethylenetriaminepentaacetic acid	5 g
Potassium sulfite	5.0×10^{-4} mole
Color developing agent (3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate)	5.5 g
Potassium carbonate	25 g
Potassium hydrogen carbonate	5 g

made up to 1 liter in total with addition of water, and adjusted pH to 10.10 with potassium hydroxide or sulfuric acid.

The same bleaching solution, fixing solution and stabilizing solution as in Example 1 were used. Consequently, substantially the same effect as in Example 2 could be obtained.

Example 4

The light-sensitive silver halide color photographic material used in Example 2 was changed to the following light-sensitive color photographic material, and further, processing steps and processing solutions were changed as shown below.

Sample II

On a paper support having one surface laminated with polyethylene and the other surface at a first layer side laminated with polyethylene containing titanium oxide, the respective layers having the following constitutions were provided by coating to prepare a multi-layer light-sensitive silver halide color photographic material (1). The coating solutions were prepared as shown below.

First layer coating solution

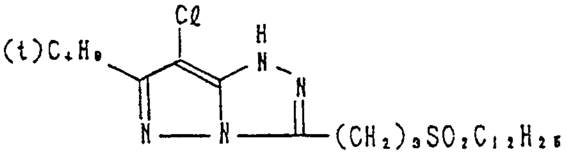
In 6.67 g of High boiling point organic solvent (DNP), 26. g of Yellow coupler (Y-1), 10.0 g of Dye image stabilizer (ST-1), 6.67 g of (ST-2) and 0.67 g of Additive (HQ-1) were dissolved with addition of 60 ml of ethyl acetate, and the solution was dispersed by emulsification in 220 ml of a 10 % aqueous gelatin solution containing 7 ml of 20 % Surfactant (SU-1) by means of an ultrasonic homogenizer to prepare a yellow coupler dispersion. This dispersion was mixed with a blue-sensitive silver halide emulsion (containing 10 g of silver) prepared under the following conditions to prepare a first layer coating solution.

The second layer to seventh layer coating solutions were prepared in the same manner as in the above first layer coating solution.

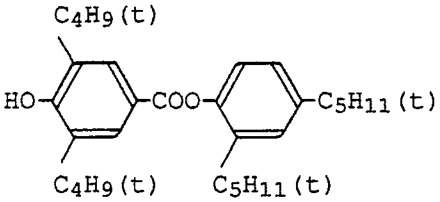
Layer	Constitution	Amount added (g/m^2)
Seventh layer (protective layer)	Gelatin	1.0
Sixth layer (UV absorbing layer)	Gelatin	0.4
	UV absorber (U-2)	0.20
	UV absorber (U-3)	0.20
	Antistaining agent (HQ-1)	0.01
	DNP	0.2
	PVP	0.03
	Antiirradiation dye (AI-2)	0.02
Fifth layer (red-sensitive layer)	Gelatin	1.30
	Red-sensitive silver chlorobromide emulsion (EmC) calculated on silver	0.21
	Cyan coupler (C-1-4)	0.17
	Cyan coupler (C-2-2)	0.25
	Dye image stabilizer (ST-1)	0.20
	Antistaining agent (HQ-1)	0.01
	HBS-1	0.20
	DOP	0.20
Fourth layer (UV-absorbing layer)	Gelatin	0.94
	UV absorber (U-2)	0.40
	UV absorber (U-3)	0.40
	Antistaining agent (HQ-1)	0.03
	DNP	0.40

Layer	Constitution	Amount added (g/m^2)
Third layer (green-sensitive layer)	Gelatin	1.40
	Green-sensitive silver chlorobromide emulsion (EmB) calculated on silver	0.17
	Magenta coupler (M-1)	0.35
	Dye image stabilizer (ST-3)	0.15
	Dye image stabilizer (ST-4)	0.15
	Dye image stabilizer (ST-5)	0.15
	DNP	0.20
	Antiirradiation dye (AI-1)	0.01
Second layer (Intermediate layer)	Gelatin	1.20
	Antistaining agent (HQ-2)	0.12
	DIDP	0.15
First layer (blue-sensitive layer)	Gelatin	1.20
	Blue-sensitive silver chlorobromide emulsion (EmA) calculated on silver	0.26
	Yellow coupler (Y-1-3)	0.80
	Dye image stabilizer (ST-1)	0.30
	Dye image stabilizer (ST-2)	0.20
	Antistaining agent (HQ-1)	0.02
	Antiirradiation dye (AI-3)	0.01
	DNP	0.20
Support	Polyethylene-laminated paper	

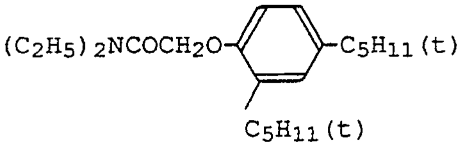
M-1



ST-1

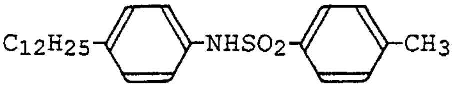


ST-2

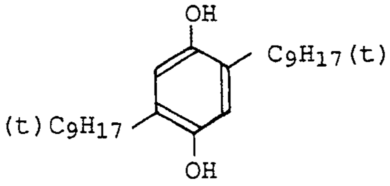


DOP: dioctyl phthalate
DIDP: diisodecyl phthalate
DNP: dinonyl phthalate
PVP: polyvinyl pyrrolidone

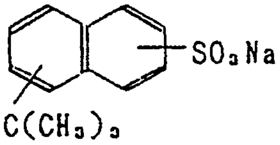
HBS-1



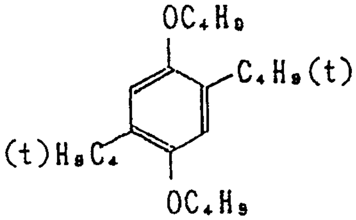
HQ-1



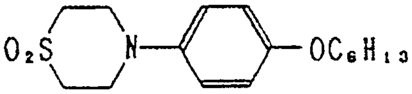
SU-1



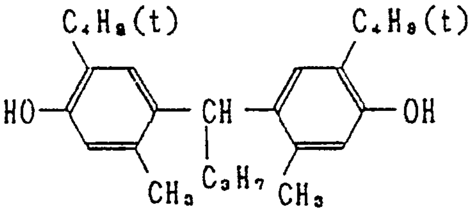
ST-3



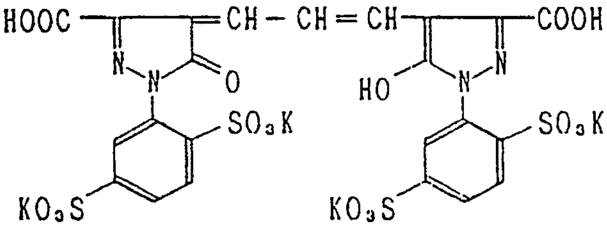
ST-4



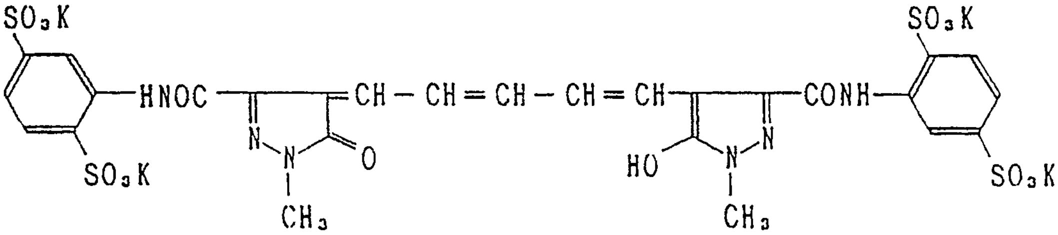
ST-5



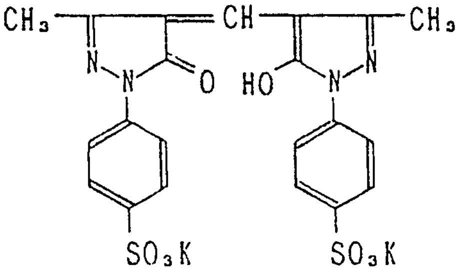
AI-1



AI-2

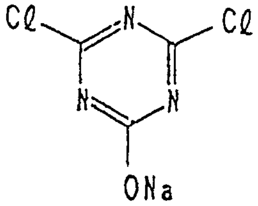


AI-3



As a hardener, the following H-1 was used.

H-1



(Preparation method of blue-sensitive silver halide emulsion)

To 1,000 ml of 2 % aqueous gelatin solution maintained at 40 °C, the following (A solution) and (B solution) were added simultaneously over 30 minutes under controlling pAg = 6.5 and pH = 3.0, and further the following (C solution) and (D solution) were added simultaneously over 180 minutes under controlling pAg = 7.3 and pH = 5.5.

During this addition, the pAg was controlled according to a method disclosed in Japanese Unexamined Patent Publication No. 45437/1984, and the pH was controlled by using an aqueous solution of sulfuric acid or sodium hydroxide.

(A solution)

Sodium chloride	3.42 g
Potassium bromide	0.03 g

made up to 200 ml with addition of water.

(B solution)

Silver nitrate	10 g

made up to 200 ml with addition of water.

(C solution)

Sodium chloride	102.7 g
Potassium bromide	1.0 g

made up to 600 ml with addition of water.

(D solution)

Silver nitrate	300 g

made up to 600 ml with addition of water.

After completion of the addition, desalting was effected by using a 5 % aqueous solution of Demol N (trade name) manufactured by Kao Atlas K.K. and a 20 % aqueous solution of magnesium sulfate, and then the solution was mixed with an aqueous gelatin solution to obtain a monodispersed cubic emulsion EMP-1 having an average grain size of 0.85 μm, coefficient of variation (σ/r) of 0.07 and a silver chloride content of 99.5 mole %.

By using the following compounds, the above emulsion EMP-1 was chemically ripened at 50 °C for 90 minutes to obtain a blue-sensitive silver halide emulsion (EmA).

Sodium thiosulfate	0.8 mg/mole of AgX
Chloroauric acid	0.5 mg/mole of AgX
Stabilizer SB-5	6×10^{-4} mole/mole of AgX
Sensitizing dye D-1	4.3×10^{-4} mole/mole of AgX
Sensitizing dye D-4	0.7×10^{-4} mole/mole of AgX

(Preparation method of green-sensitive silver halide emulsion)

The procedures were carried out in the same manner as in EMP-1 except for changing the addition time of (A solution) and (B solution) and the addition time of (C solution) and (D solution) to obtain a monodispersed cubic emulsion EMP-2 having an average grain size of 0.43 μm, coefficient of variation (σ/r) of 0.08 and a silver chloride content of 99.5 mole %.

By using the following compounds, the above emulsion EMP-2 was chemically ripened at 55 °C for 120 minutes to obtain a green-sensitive silver halide emulsion (EmB).

Sodium thiosulfate	1.5 mg/mole of AgX
Chloroauric acid	1.0 mg/mole of AgX
Stabilizer SB-5	6×10^{-4} mole/mole of AgX
Sensitizing dye D-2	4×10^{-4} mole/mole of AgX

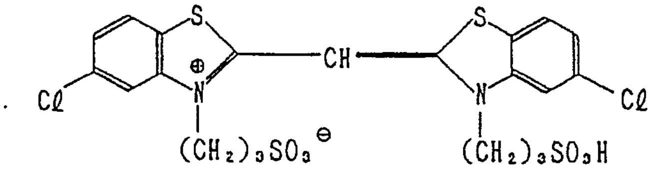
(Preparation method of red-sensitive silver halide emulsion) ·

The procedures were carried out in the same manner as in EMP-1 except for changing the addition time of (A solution) and (B solution) and the addition time of (C solution) and (D solution) to obtain a monodispersed cubic emulsion EMP-3 having an average grain size of 0.50 μm, coefficient of variation (σ/r) of 0.08 and a silver chloride content of 99.5 mole %.

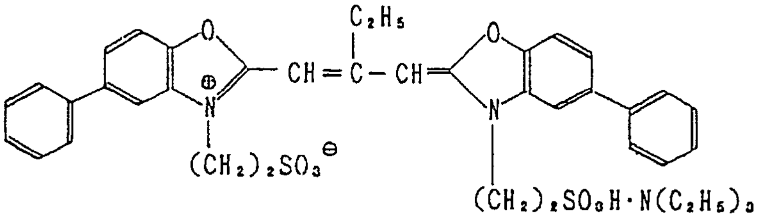
By using the following compounds, the above emulsion EMP-3 was chemically ripened at 60 °C for 90 minutes to obtain a red-sensitive silver halide emulsion (EmC).

Sodium thiosulfate	1.8 mg/mole of AgX
Chloroauric acid	2.0 mg/mole of AgX
Stabilizer SB-5	6×10^{-4} mole/mole of AgX
Sensitizing dye D-3	1.0×10^{-4} mole/mole of AgX

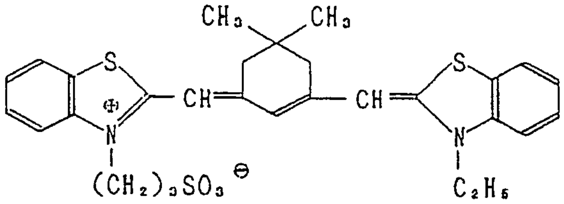
D－1



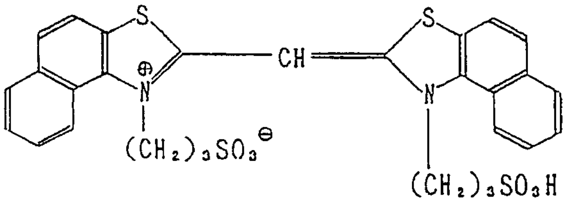
D－2



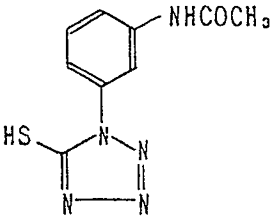
D－3



D－4



SB－5



After the samples obtained were subjected to exposure according to a conventional method, the same evaluation as in Example 2 was made by using the following processing steps and processing solutions.

(1) Color Development	35.0 ± 0.3 °C	45 sec
(2) Bleaching	35.0 ± 0.5 °C	30 sec
(3) Fixing	35.0 ± 0.5 °C	30 sec
(4) Stabilizing (3 tank cascade)	30 to 34 °C	90 sec
(5) Drying	60 to 80 °C	30 sec

(Color developing tank solution)
the same color developing solution used in Example 3.

(Bleaching and fixing solutions) the same solutions used in Example 1.

(Stabilizing solution)

Orthophenylphenol	0.1 g
Yubitex (trade name, manufactured by Ciba Geigy Co.)	0.5 g
$ZnSO_4 \cdot 7H_2O$	0.15 g
Ammonium sulfite (40 % solution)	4.5 ml
1-Hydroxyethylidene-1,1-diphosphonic acid (60 % solution)	2.0 g
Ethylenediaminetetraacetic acid	1.0 g

made up to 1 liter with water, and adjusted pH to 7.5 with aqueous ammonia or sulfuric acid.

Consequently, substantially the same results as in Example 2 were obtained. Although stain was slightly more liable to be generated as compared with the light-sensitive silver halide color photographic material in Example 1, stain generation could be prevented effectively by lowering the rate of an ammonium salt in total cations as described above.

Example 5

The evaluation was made in the same manner as in Example 1 except for changing the color developing agent of the color developing solution in Example 1 to 3-methyl-4-amino-N-ethyl-N(β-methanesulfonamidoethyl)-aniline sulfate.

The results are shown in Table 3.

Table 3

Experiment No.	Ferric organic acid complex salt	Amount added (mole/ℓ)	pH	Yellow density of unexposed portions
1-1	EDTA·Fe	0.30	4.5	0.62
1-2	NTA·Fe	0.30	4.5	0.61
1-3	CyDTA·Fe	0.30	4.5	0.61
1-4	EDTMP·Fe	0.30	4.5	0.62
1-5	NTMP·Fe	0.30	4.5	0.62
1-6	(A-1)·Fe	0.30	4.5	0.62
1-7	(A-4)·Fe	0.30	4.5	0.62
1-8	(A-7)·Fe	0.30	4.5	0.63
1-9	(A-9)·Fe	0.30	4.5	0.61
1-10	(A-1)·Fe	0.05	4.5	0.59
1-11	(A-1)·Fe	0.10	4.5	0.61
1-12	(A-1)·Fe	0.19	4.5	0.61
1-13	(A-1)·Fe	0.23	4.5	0.62
1-14	(A-1)·Fe	0.40	4.5	0.62
1-15	(A-1)·Fe	0.50	4.5	0.63
1-16	(A-1)·Fe	0.60	4.5	0.65
1-17	(A-1)·Fe	0.30	1.5	0.58
1-18	(A-1)·Fe	0.30	2.0	0.58
1-19	(A-1)·Fe	0.30	3.0	0.59
1-20	(A-1)·Fe	0.30	4.0	0.59
1-21	(A-1)·Fe	0.30	5.0	0.59
1-22	(A-1)·Fe	0.30	5.5	0.62
1-23	(A-1)·Fe	0.30	6.0	0.66
1-24	(A-1)·Fe	0.30	7.0	0.73

As clearly shown in the results in Table 3, by changing a color developing agent from 4-amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)aniline sulfate (hereinafter called "CD-4") to 3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate (hereinafter called "CD-3"), bleaching fog is slightly lowered even though tendency of yellow stain generation is not so changed, whereby it can be said to be a preferred embodiment in the present invention.

Example 6

By using the light-sensitive color material used in Example 1, running processing was carried out by the following processing solutions.

(Color developing solution) the color developing solution used in Example 1.

(Color developing replenishing solution)

Potassium carbonate	35 g
Sodium hydrogen carbonate	3 g
Potassium sulfite	5 g
Sodium bromide	0.5 g
Hydroxylamine sulfate	3.1 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate	5.8 g
Potassium hydroxide	2 g
Diethylenetriaminepentaacetic acid	1.5 g

made up to 1 liter with addition of water, and adjusted pH to 10.12 with potassium hydroxide or 20 % sulfuric acid.

(Bleaching solution)

Ferric organic acid potassium salt (shown in Table 4)	0.3 mole
Disodium ethylenediaminetetraacetate	5.0 g
Potassium bromide	150 g
Glacial acetic acid	40 ml
Potassium nitrate	30 g

made up to 1 liter with addition of water, controlled a rate of an ammonium salt in total cations as shown in Table 4, and adjusted pH to 4.2.

The bleaching replenishing solution used had the following composition.

Ferric organic acid potassium salt	0.32 mole
Disodium ethylenediaminetetraacetate	2 g
Potassium bromide	178 g
Glacial acetic acid	50 ml
Potassium nitrate	30 g

made up to 1 liter with addition of water, controlled a rate of an ammonium salt in total cations as shown in Table 4, and adjusted pH to 3.5.

The fixing solution used had the following composition.

Sodium thiosulfate	100 g
Potassium thiocyanate	150 g
Anhydrous sodium bisulfite	12 g
Sodium metabisulfite	2.5 g
Disodium ethylenediaminetetraacetate	0.5 g

made up to 1 liter with addition of water, and adjusted pH to 6.5 with diethanolamine or acetic acid.

The fixing replenishing solution used had the following composition.

Potassium thiosulfate	130 g
Potassium thiocyanate	190 g
Anhydrous sodium bisulfite	15 g
Sodium metabisulfite	3 g
Disodium ethylenediaminetetraacetate	0.8 g

made up to 1 liter with addition of water, and adjusted pH to 6.5.

As a stabilizing replenishing solution, the stabilizing solution in Example 1 was used.

The processing steps, processing time, processing temperature and replenishing amount of the running processing are as shown below.

Processing step	Processing time	Processing temperature	Replenishing amount
Color developing	3 min 15 sec	38 °C	540 ml
Bleaching	35 sec	38 °C	200 ml
Fixing	1 min 10 sec	38 °C	860 ml
Stabilizing	50 sec	38 °C	860 ml
Drying	1 min	40 to 70 °C	-

(the replenishing amount is a value per 1 m^2 of the light-sensitive material.)

The running processing was carried out until the amount of the bleaching replenishing solution twice as much as the the bleaching tank volume was replenished. The yellow densities at unexposed portions and amounts of residual silver at maximum density portions after completion of the running processing were measured..

The results are shown together in Table 4.

Table 4

Experiment No.	Ferric organic acid potassium salt	Rate of ammonium salt (mole %)	Yellow density at unexposed portion	Amount of residual silver (mg/100 cm^2)
4-1	EDTA·Fe	80	0.65	8.3
4-2	EDTA·Fe	60	0.64	8.6
4-3	EDTA·Fe	50	0.63	9.0
4-4	EDTA·Fe	20	0.62	9.4
4-5	EDTA·Fe	0	0.62	10.5
4-6	(A-1)·Fe	80	0.75	0.2
4-7	(A-1)·Fe	60	0.70	0.3
4-8	(A-1)·Fe	50	0.66	0.3
4-9	(A-1)·Fe	20	0.64	0.3
4-10	(A-1)·Fe	0	0.63	0.3
4-11	(A-9)·Fe	80	0.73	0.3
4-12	(A-9)·Fe	60	0.68	0.4
4-13	(A-9)·Fe	50	0.65	0.4
4-14	(A-9)·Fe	20	0.64	0.4
4-15	(A-9)·Fe	0	0.64	0.4

As clearly shown in Table 4, it can be understood that also in the running processing, by lowering the rate of an ammonium salt in total cations, bleaching fog are prevented effectively.

Example 7

The same evaluation as in Example 6 was made except for using Experiments No. 4-1, No. 4-5, No. 4-6 and No. 4-10 in Example 6 and changing the replenishing amounts of the bleaching solution as shown in Table 5.

The results are shown in Table 5.

Table 5

Experiment No.	Bleaching solution No. (No. in Example 6)	Replenishing amount of bleaching solution (ml/m^2)	Yellow density at unexposed portions	Amount of residual silver (mg/100 cm^2)
5-1	4-1	450	0.64	7.8
5-2	4-1	400	0.64	8.0
5-3	4-1	200	0.65	8.3
5-4	4-1	100	0.66	9.2
5-5	4-5	450	0.61	8.5
5-6	4-5	400	0.61	9.2
5-7	4-5	200	0.62	10.5
5-8	4-5	100	0.64	12.1
5-9	4-6	450	0.67	0.2
5-10	4-6	400	0.68	0.3
5-11	4-6	200	0.73	0.3
5-12	4-6	100	0.78	0.3
5-13	4-10	450	0.62	0.2
5-14	4-10	400	0.62	0.2
5-15	4-10	200	0.63	0.3
5-16	4-10	100	0.65	0.3

As clearly shown in Table 5, it can be understood that when the replenishing amount of the bleaching solution is reduced, yellow stain will be generated easily, but when the bleaching solution of the present invention is used, increase in bleaching fog is prevented in spite of the replenishing amount, and therefore the effect of the present invention is exhibited remarkably when the replenishing amount of the bleaching solution is reduced.

Example 8

By using the color paper in Example 4, the same evaluation as in Example 7 was made by using the following processing steps and processing solutions.

(Processing steps) the same processing steps used in Example 4

(Color developing tank solution)

Triethanolamine	10 g
Ethylene glycol	6 g
Cinopal SFP (trade name, manufactured by Ciba Geigy Co.)	1 g
Yubitex MST (trade name, manufactured by Ciba Geigy Co.)	1 g
N,N-Diethylhydroxylamine	3.6 g
Potassium bromide	20 mg
Potassium chloride	2.5 g
Diethylenetriaminepentaacetic acid	5 g
Potassium sulfite	5.0×10^{-4} mole
Color developing agent (3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate)	5.5 g
Potassium carbonate	25 g
Potassium hydrogen carbonate	5 g

made up to 1 liter in total with addition of water, and adjusted pH to 10.10 with potassium hydroxide or sulfuric acid.

(Color developing replenishing solution)

Triethanolamine	14.0 g
Ethylene glycol	8.0 g
Cinopal SFP (trade name, manufactured by Ciba Geigy Co.)	1.2 g
Yubitex MST (trade name, manufactured by Ciba Geigy Co.)	1.5 g
N,N-Diethylhydroxylamine	5 g
Potassium bromide	8 mg
Potassium chloride	0.3 g
Diethylenetriaminepentaacetic acid	7.5 g
Potassium sulfite	7.0×10^{-4} mole
Color developing agent (3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate)	8 g
Potassium carbonate	30 g
Potassium hydrogen carbonate	1 g

made up to 1 liter in total with addition of water, and adjusted pH to 10.40 with potassium hydroxide or sulfuric acid.

(Bleaching solution and bleaching replenishing solution)

Ferric organic acid potassium salt	0.15 mole
Disodium ethylenediaminetetraacetate	1.0 g
Potassium bromide	50 g
Glacial acetic acid	20 ml
Potassium nitrate	30 g

made up to 1 liter with addition of water, and adjusted pH to 4.5.

(Fixing solution and fixing replenishing solution)

Potassium thiosulfate	70 g
Potassium thiocyanate	20 g
Sodium sulfite	15 g
Disodium ethylenediaminetetraacetate	0.5 g

made up to 1 liter with addition of water, and adjusted pH to 6.0.

(Stabilizing solution and stabilizing replenishing solution)

The stabilizing solution described in Example 4.

The replenishing amounts of the respective processing solutions were 60 ml/m^2 of the color developing solution, 30 ml/m^2 of the bleaching solution, 60 ml/m^2 of the fixing solution and 250 ml/m^2 of the stabilizing solution per 1 m^2 of the light-sensitive color material. The same evaluation as in Example 7 was made to obtain substantially the same tendency as in Example 7.

Example 9

Experiment was carried out in the same manner as in Example 6 except for providing a nozzle made of vinyl chloride having perforations with a diameter of 5 mm in the bleaching processing tank and the fixing processing tank, spraying the processing solutions on an emulsion surface of the light-sensitive material by means of Iwaki Magnet Pump MD-15 (trade name, manufactured by Iwaki Co.), and further changing crossover time between the color developing tank and the bleaching tank from 8 seconds to 5 seconds. As a result, the yellow density at unexposed portions was further lowered by 0.01 to 0.02, and the amount of residual silver was reduced by half.

Example 10

By using the samples in which Yellow coupler Y-2 in Sample I and Yellow coupler Y-1-3 in Sample II were changed to equimolar amounts of yellow couplers shown in Table 6, respectively, processings were carried out by using the processing steps and processing solutions in Example 6 or Example 8, respectively, and yellow densities at unexposed portions were measured.

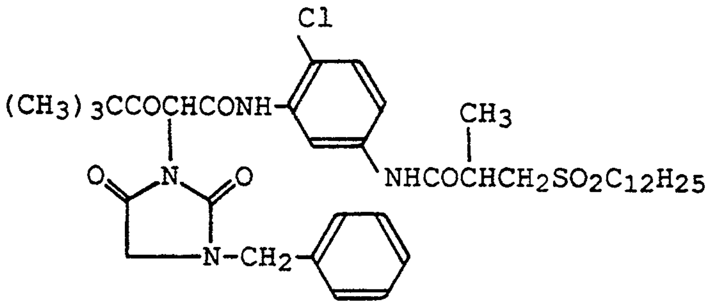
However, since the bleaching agent of the bleaching solution used was (A-1)•Fe with the rate of an ammonium salt being 0, a processing solution of which the pH was adjusted by triethanolamine or acetic acid was used. Sample I was measured by a transmission density, and Sample II was measured by a reflection density.

The results are shown in Table 6.

Table 6

Experiment No.	Sample	Yellow coupler	Yellow density at unexposed portions
6-1	Sample I	YB-16	0.61
6-2	Sample I	YB-17	0.61
6-3	Sample I	YB-18	0.62
6-4	Sample I	YB-19	0.62
6-5	Sample I	YB-20	0.61
6-6	Sample II	Y-1-1	0.07
6-7	Sample II	Y-1-9	0.07
6-8	Sample II	Y-1-10	0.06
6-9	Sample II	Y-1-16	0.06
6-10	Sample II	Y-1-51	0.07

YR-1



As clearly shown in Table 6, in Sample I and Sample II, by changing a yellow coupler to the yellow coupler preferred for practicing the present invention, yellow stain was reduced and bleaching fog was reduced by about 0.01 to 0.03.

However, in Sample II, when YR-1 coupler is used, the yellow density becomes 0.08.

Additionally, in YB-21, YB-22, YB-23 and YB-32, the above effect was also recognized.

Example 11

By using the samples in which Magenta couplers M'-2 and M'-3 in Sample I and Magenta coupler M-1 in Sample II were changed to equimolar amounts of magenta couplers shown in Table 7, respectively, processings were carried out by using the processing steps and processing solutions in Example 6 or Example 8, respectively, and magenta densities at unexposed portions were measured. The bleaching solution having the composition described in Example 10 was used.

The results are shown in Table 7.

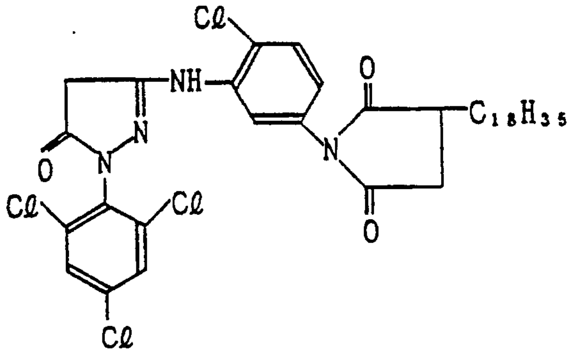
Table 7

Experiment No.	Sample	Magenta coupler	Magenta density at unexposed portions
7-1	Sample I	M'-2/M'-3	0.59
7-2	Sample I	M-1	0.58
7-3	Sample I	M-2	0.58
7-4	Sample I	M-4	0.57
7-5	Sample I	M-10	0.58
7-6	Sample I	M-60	0.58
7-7	Sample I	M-74	0.58
7-8	Sample II	MR-1	0.07
7-9	Sample II	M-23	0.05
7-10	Sample II	M-32	0.06
7-11	Sample II	M-39	0.06
7-12	Sample II	M-61	0.06
7-13	Sample II	M-63	0.06
7-14	Sample II	M-64	0.06

As clearly shown in Table 7, it can be understood that in Sample I and Sample II, by changing a magenta coupler to the magenta coupler preferred for practicing the present invention, magenta stain at unexposed portion was reduced.

In addition to the magenta couplers shown in Table 7, M-20, M-21, M-31, M-46, M-76, M-78 and M-81 were examined, and substantially the same results as shown in Table 7 were obtained.

MR-1



Example 12

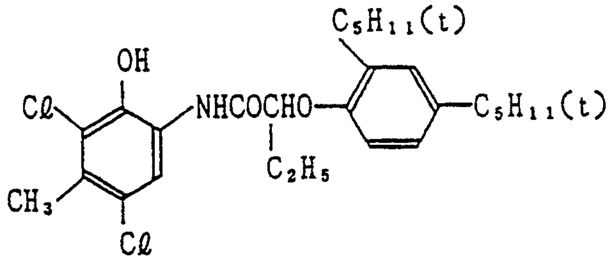
By using the samples in which Cyan couplers C'-2 and C'-3 in Sample I and Cyan coupler C-2-2 in Sample II were changed to equimolar amounts of cyan couplers shown in Table 8, respectively, processings were carried out by using the processing steps and processing solutions in Example 6 or Example 8, respectively, and cyan densities at unexposed portions were measured. The bleaching solution having the composition described in Example 10 was used.

The results are shown in Table 8.

Table 8

Experiment No.	Sample	Cyan coupler	Cyan density at unexposed portions
8-1	Sample I	C'-3/C'-2	0.22
8-2	Sample I	C-1	0.21
8-3	Sample I	C-2	0.21
8-4	Sample I	C-3	0.21
8-5	Sample I	C-8	0.20
8-6	Sample I	C-32	0.21
8-7	Sample I	C-36	0.21
8-8	Sample I	C-70	0.21
8-9	Sample I	C-72	0.21
8-10	Sample I	C-79	0.21
8-11	Sample I	C-20	0.20
8-12	Sample I	C-22	0.20
8-13	Sample I	C-30	0.20
8-14	Sample I	C-33	0.21
8-15	Sample II	CR-1	0.05
8-16	Sample II	C-2-2	0.03
8-17	Sample II	C-2-18	0.03
8-18	Sample II	C-2-24	0.03
8-19	Sample II	C-2-27	0.03
8-20	Sample II	C-1-10	0.03

CR-1



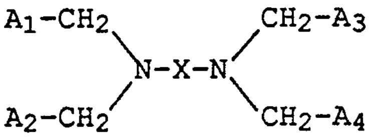
As clearly shown in Table 8, it can be understood that by using the cyan coupler preferred for practicing the present invention, cyan stain was reduced slightly.

Example 13

By pouring the bleaching solution, the fixing solution and the stabilizing solution other then the color developing solution used in Example 6 and an overflow solution at the time of the running processing in Example 6 into the tank for processing the color paper in Example 8, processings were carried out continuously without replenishment. As a result, although stain on the color paper was high by about 0.01 as compared with the case when Y, M and C were replenished without pouring, the amount of waste liquor was reduced by about half, and therefore this is a preferred embodiment in the point of low pollution.

Claims

1. A bleaching solution for a light-sensitive silver halide color photographic material comprising at least 0.10 mole/ℓ of a ferric complex salt of a compound represented by the following formula (A) and 50 mole % or less of total cations being ammonium ions.



(A)

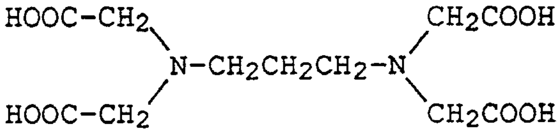
wherein A_1 to A_4 may be the same or different, respectively and represent $-CH_2OH$, $-COOM$ or $-PO_3M_1M_2$ where M, M_1 and M_2 each represent a hydrogen atom, sodium, potassium or ammonium; and X represents a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms and a total carbon number including a branched portion is 3 or more.

2. The solution of Claim 1 wherein said bleaching solution has a pH of 2.0 to 5.5.

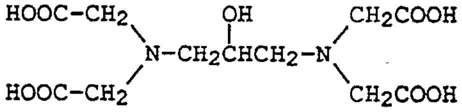
3. The solution of Claim 1 wherein an amount of the ammonium ion is 20 mole % or less based on the total cations.

4. The solution of Claim 1 wherein said compound represented by the formula (A) is selected from the group consisting of:

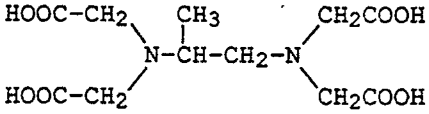
(A - 1)



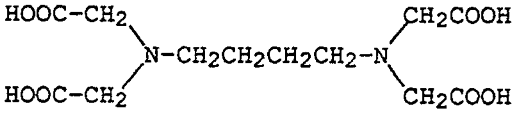
(A - 2)



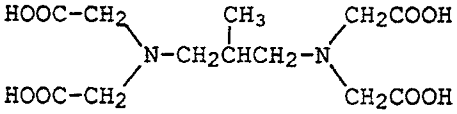
(A - 3)



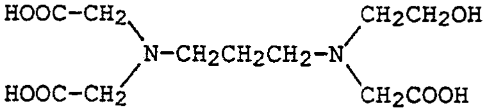
(A - 4)



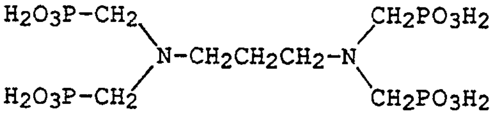
(A - 5)



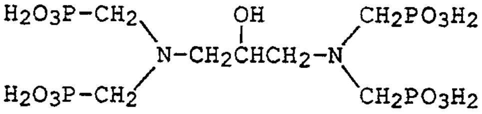
(A - 6)



(A - 7)

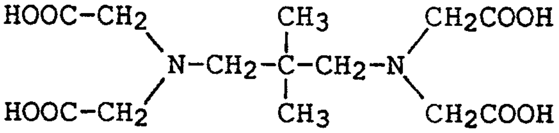


(A - 8)



and

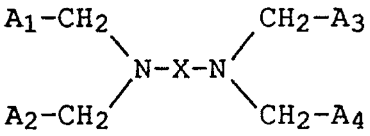
(A - 9)



.

5. The solution of Claim 4 wherein the compound is contained in an amount of 0.15 mole to 0.6 mole per liter of the solution.

6. A method for processing a light-sensitive silver halide color photographic material in which a light-sensitive silver halide color photographic material is subjected to imagewise exposure, processed by a color developing solution, and immediately thereafter processed by a bleaching solution, characterized in that 50 mole % or less of total cations in said bleaching solution are ammonium ions, and said bleaching solution contains at least 0.10 mole/ℓ of a ferric complex salt of a compound represented by the formula (A).



(A)

wherein A_1 to A_4 may be the same or different, respectively and represent $-CH_2OH$, $-COOM$ or $-PO_3M_1M_2$ where M, M_1 and M_2 each represent a hydrogen atom, sodium, potassium or ammonium; and X represents a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms and a total carbon number including a branched portion is 3 or more.

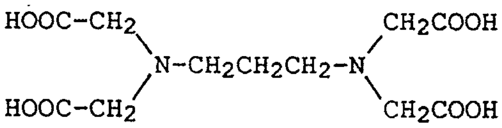
7. The method of Claim 6 wherein said bleaching solution has a pH of 2.0 to 5.5.

8. The method of Claim 6 wherein ammonium ion is contained in an amount of 20 mole % or less based on the total cations in the bleaching solution,.

9. The method of Claim 6 wherein a replenishing amount of said bleaching solution is 20 to 400 ml per 1 m^2 of a light-sensitive silver halide color photographic material.

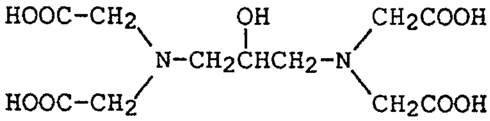
10. The method of Claim 6 wherein said compound represented by the formula (A) is selected from the group consisting of:

(A - 1)



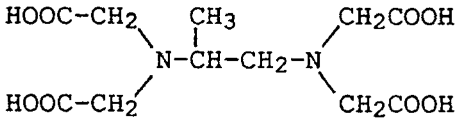
$(HOOC-CH_2)_2N-CH_2CH_2CH_2-N(CH_2COOH)_2$

(A - 2)



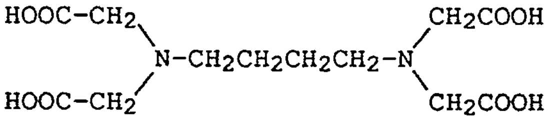
$(HOOC-CH_2)_2N-CH_2CH(OH)CH_2-N(CH_2COOH)_2$

(A - 3)



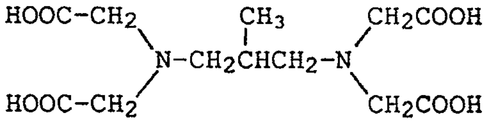
$(HOOC-CH_2)_2N-CH(CH_3)-CH_2-N(CH_2COOH)_2$

(A - 4)



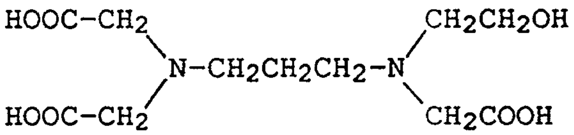
$(HOOC-CH_2)_2N-CH_2CH_2CH_2CH_2-N(CH_2COOH)_2$

(A - 5)

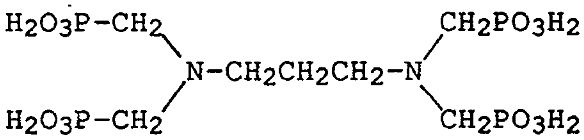


$(HOOC-CH_2)_2N-CH_2CH(CH_3)CH_2-N(CH_2COOH)_2$

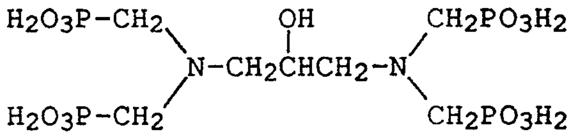
(A - 6)



(A - 7)

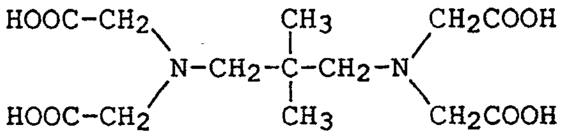


(A - 8)



and

(A - 9)



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