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

(11) Publication number: **0 243 100**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **87303370.8**

(22) Date of filing: **15.04.87**

(51) Int.Cl.³: **G 03 C 7/30**

(30) Priority: **19.04.86 JP 91106/86**
19.04.86 JP 91107/86

(43) Date of publication of application:
28.10.87 Bulletin 87/44

(84) Designated Contracting States:
DE GB

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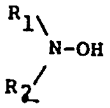
(54) Color developing solution for processing light-sensitive silver halide color photographic material and method employing the same.

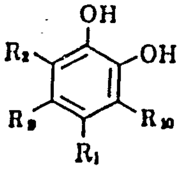
(57) Dislosed is a color developing solution for processing a light-sensitive silver halide color photographic material, which comprises the compound represented by General Formula (I) shown below and at least one selected from the group consisting of the compounds represented by General Formula (II) and (III) shown below:

General Formula (I)

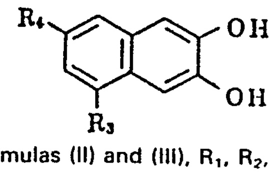


wherein R_1 and R_2 each represent an alkyl group having 1 to 3 carbon atoms,

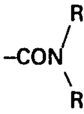
General Formula (II)



General Formula (III)



wherein, in Formulas (II) and (III), R_1, R_2, R_3, R_4, R_9 and R_{10} each represent a hydrogen atom, a halogen atom, a sulfonic acid group, an alkyl group having 1 to 7 carbon atoms, $-OR_5$, $-COOR_6$,



$-CON(R_7)(R_8)$, or a phenyl group,

wherein R_5, R_6, R_7 and R_8 each represent a hydrogen atom or an alkyl group having 1 to 18 carbon atoms.

This invention can provide a color developing solution for a processing light-sensitive silver halide color photographic material and a method employing the same being excellent in photographic performance for fog and maximum density.

EP 0 243 100 A2

Croydon Printing Company Ltd

Color developing solution for processing light-sensitive silver halide color photographic material and method employing the same

BACKGROUND OF THE INVENTION

This invention relates to a color developing solution for and a method of processing a light-sensitive silver halide color photographic material, and, more particularly, it relates to a color developing solution for and a method of processing a light-sensitive silver halide color photographic material being excellent in the photographic performances for fog and maximum density.

In the method of forming dye images by processing light-sensitive silver halide color photographic materials, the dye images are usually formed, after imagewise exposure, by reacting an oxidized p-phenylenediamine type color developing agent with a dye image-forming coupler. In such a method, a color reproduction method according to the subtractive color process is usually used to form dye images of cyan, magenta and yellow respectively corresponding to red, green and blue. Recent years, in the formation of such dye images, it is generally practiced to carry out a high temperature developing and simplify processing steps in order to achieve a shortened developing processing time. In particular, in order to achieve the shortened developing processing time, it becomes very important to increase the developing speed in color development. The developing speed in color development is governed from two approaches. One of them is a light-sensitive silver halide color photographic material, and the other of them is a color developing solution. In the former, the composition of the grains in a silver halide emulsion to be used may give great influence to the developing speed, and, in the latter, the conditions or composition of the color developing solution may give great influence to the developing speed.

In the prior art, there have been employed hydroxylamines and sulfites as preservative of the color developing solution. In particular, hydroxylamines are effective as the preservative for p-phenylenediamine type color developing solution.

However, there are drawbacks that hydroxylamines are decomposed by oxidization and results in generation of ammonia NH_3. The genarated ammonia NH_3 acts with light-sensitive silver halide photographic material and causes ammonia fog on the light-sensitive material.

Particularly, hydroxylamines become to be further decomposable by the presence of heavy metal ions (e.g., Fe^{3+}, Cu^{2+}, etc.) contained in the color developing solution.

Various chelating agents have been inspored and prodiced in order to chelate the heavy metal ions and inhibit their acts. As these chelating agents, there may be exemplified aminopolycarbonic acid, polyphosphoric acid, organic phosphoric acid, etc. However, although these chelating agents are effective for Fe^{3+}, they are less effective for Cu^{2+}.

Also, concentrations of Cu^{2+} and Fe^{3+} in the color developing solution is liable to become higher by the recent tendency to lower the replenishment of the color developing solution economy or shortening the waste solution. Therefore, it is increasingly desired to dissolve the above drawbacks.

On the other hand, the light-sensitive silver halide color photographic materials wherein a light-sensitive silver halide emulsion is substantially comprised of silver chloride (hereinafter referred to as light-sensitive silver chloride color photographic materials) can be rapidly developed as compared with conventional light-sensitive color photographic materials comprising a silver halide emulsion containing silver bromides or silver iodides such as silver chlorobromide, silver chloroiodobromide and silver iodobromide, and moreover can be free from accumulation in the color developing solution, of bromide ions or iodide ions which are susceptible to suppress development reactions. Thus, they are very useful as light-sensitive materials for a rapid processing. The present inventors have made various studies by using light-sensitive silver chloride color photographic materials suited for use in the rapid processing, and, as a result, find that the materials have the following disadvantages.

That is, as a first instance, the above-mentioned hydroxylamine conventionally used as one of preservatives tends to act as a developing agent for the silver chloride so that the silver development may proceed, to lower color density of color images finally obtained.

As a second instance, the above-mentioned sulfite conventionally used as other preservatives tends to act as a dissolving agent for the silver chloride so that the physical development due to a color developing agent may rapidly proceed, to lose the balance between the silver development reaction and the coupling reaction; in other words, the silver development may overly precede and the coupling reaction may delay, whereby the color density is lowered.

According to the present inventor's studies, it was also found that fog is liable to appear especially when the solution is contaminated with a heavy metal ion.

This fog may largely appear as a whole, and particularly largely has appeared in cyan color used for the purpose of preventing the decrease in color density.

This heavy metal ion may raise a problem especially when a large quantity of light-sensitive materials is continuously processed.

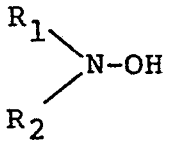
In a processing method of continuously processing light-sensitive silver halide color photographic materials by use of an automatic processor and the like, it is also necessary to take a measure for keeping components in a color developing solution in the range of predetermined concentration in order to prevent the change in the development finishing performance due to the change in the concentration of the components. As such a measure, there has been usually used a method in which a replenishing solution is supplied to replenish short components and dilute unnecessary increased components. Supplying such a replenishing solution may bring about an overflow in a large quantity, which must be abandoned, throwing a great problem from an economical viewpoint and an environmental viewpoint. For this reason, in recent years, the so-called concentrated low replenishing system wherein the replenishing solution is made to have a higher concentration and supplied in a small quantity has been extensively used in order to decrease the above overflow solution. In such a system, however, heavy metal ions are liable to be accumulated, thereby raising the above problem of fog due to heavy metal ions. It has thus been sought after to solve these problems.

SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide a color developing solution which can inhibit ammonia fog and effect chelating of heavy metal ions and does not cause excess development even when light-sensitive silver chloride color photographic material is employed, and a method employing the color developing solution.

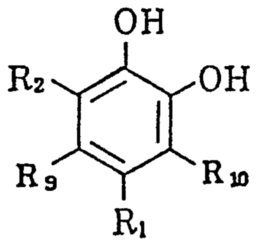
The above object of this invention can be achieved by a color developing solution comprising the compound represented by General Formula (I) shown below and at least one compound selected from the compounds represented by General Formulas (II) and (III) shown below:

General Formula (I)

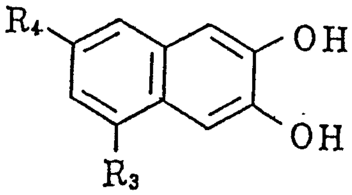


wherein R_1 and R_2 each represent an alkyl group having 1 to 3 carbon atoms,

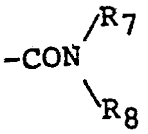
General Formula (II)



General Formula (III)



wherein, in Formulas (II) and (III), R_1, R_2, R_3, R_4, R_9 and R_{10} each represent a hydrogen atom, a halogen atom, a sulfonic acid group, an alkyl group having 1 to 7 carbon atoms, $-OR_5$, $-COOR_6$,



$-CON\begin{matrix} / R_7 \\ \backslash R_8 \end{matrix}$, or a phenyl group,

wherein R_5, R_6, R_7 and R_8 each represent a hydrogen atom or an alkyl group having 1 to 18 carbon atoms,

or by a method of processing a light-sensitive silver halide color photographic material having at least one silver halide emulsion layer, which comprises, after imagewise exposure of a light-sensitive silver halide color photographic material, carrying out processing including at least a color developing step by employing the color developing solution.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

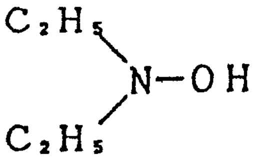
In the color developing solution used in this invention, the compound represented by General Formula (I) (hereinafter called the preservative of this invention) is used in place of hydroxylamine conventionally used as a preservative.

In General Formula (I), R_1 and R_2 each represent an alkyl group having 1 to 3 carbon atoms, and the alkyl group having 1 to 3 carbon atoms represented by R_1 and R_2 may be the same or different, including, for example, a methyl group, an ethyl group a n-propyl group, an iso-propyl group, etc.

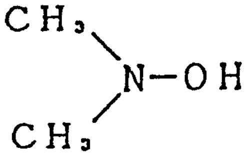
R_1 and R_2 are preferably both an ethyl group.

Specific examples of the compound represented by General Formula (I) are shown below, but this invention is by no means limited to these.

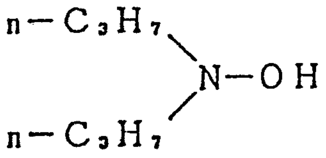
(I－1)



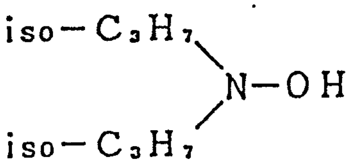
(I－2)



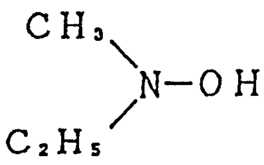
(I－3)



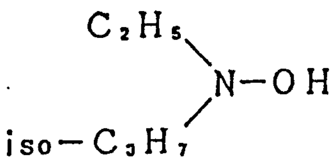
(I－4)



(I－5)



(I－6)



These compounds of this invention are usually used in the form of salts such as hydrochloride, sulfate, p-toluenesulfonate, oxalate, phosphate and acetate.

Concentration of the compound (I) of this invention in the color developing solution may be approximately the same as the concentration of the hydroxylamine usually used as a preservative, and it may be used preferably in concentration of 0.1 g/lit. to 50 g/lit., more preferably 0.5 g/lit. to 30 g/lit.

Of the compound represented by General Formula (I) in this invention, N,N-diethylhydroxylamine, for example, is known to be used as a preservative of a black and white developing agent in a color developing solution to which a black and white developing agent is added.

It is known that usually the black and white developing agent, i.e., hydroquinone, hydroquinonemonosulfonic acid, phenidone, p-aminophenol, etc. is relatively stable when used as the black and white developing agent in the black and white developing solution, and can be sufficiently preserved by using sulfite as a preservative, but, once it is added to a color developing solution, there takes place a cross oxidation reaction with a color developing agent, resulting in its very poor storage stability. Hydroxylamine is hardly effective for the preservation of the black and white developing agent added to such a color developing solution.

As an example in which N,N-diethylhydroxylamine is used as a preservative of the black and white developing agent added to a color developing solution, it is known to use it together with phenidone in the so-called external color process, which is a process by which a light-sensitive color photographic material is developed according to a reversal process by using a color developing solution containing a coupler. In such an instance, a role of the phenidone is to increase the developing speed of the light-sensitive material of external system having poor developing performance and to increase the density of a dye image.

In, for example, a magenta color developing solution containing such phenidone, N,N-diethylhydroxylamine is also known to adversely affect the preservativity of the color developing solution of external system as it destroys the coupler (see Japanese Patent Publication No. 22198/1970).

As other example in which the compound of this invention such as N,N-diethylhydroxylamine or the like is used as a preservative of the black and white developing agent in a color developing solution, reference can be made to a technique by which a phenidone derivative added to a color developing agent is preserved (see Japanese Unexamined Patent Publication No. 32035/1978) or a technique.by which a phenidone derivative is similarly preserved together with hydroquinones (see Japanese Unexamined Patent Publication No. 153437/1977).

As mentioned above, the compound of this invention has been conventionally known to be used as a preservative of the black and white developing agent added to a color developing solution, but has not been known as a preservative of a color developing agent in an ordinary color developing solution.

Thus, a part of the compound of this invention has been already known as a preservative of the black and white developing agent added to a color developing solution. However, in this invention, not only the compound (I) can effectively act as a preservative of an ordinary color developing solution, but also the color density may not be lowered even when used in combination with a particular coupler shown below, and, by using the compound in combination with a chelating agent or agents represented by General Formula (II) and/or General Formula (III), generation of fog due to the contamination with heavy metals can be desirably prevented, and further, there can be obtained a developing solution having excellent stability without fall of pH and formation of tar. These are surprising effects that can not be expected at all.

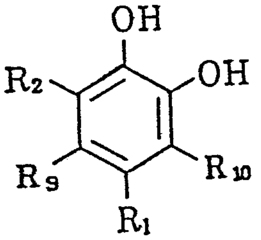
One of the conditions for the color developing solution used in this invention is to contain the sulfite in concentration of 2×10^{-2} mole or less, preferably 4×10^{-3} or less, per 1 liter of the color developing solution.

In this invention, it is preferable to lower the concentration of the above sulfite below a constant value, because it can further inhibit the lowering of the color density of color image and accomplish the effect of this invention more effectively.

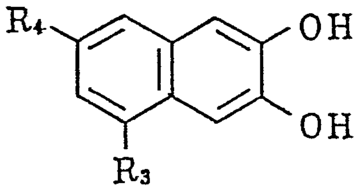
The sulfite used in this invention may include sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, etc.

The color developing agent used in this invention contains at least one compound selected from the compound represented by General Formula (II) and the compound represented by General Formula (III) (hereinafter referred to as the chelating agent of this invention).

General Formula (II)



General Formula (III)



In General Formulas (II) and (III), R_1, R_2, R_3, R_4, R_9 and R_{10} each represent a hydrogen atom, a halogen atom, a sulfonic acid group, an alkyl group having 1 to 7 carbon atoms, $-OR_5$, $-COOR_6$,

$$-CON\begin{matrix}/R_7\\ \backslash R_8\end{matrix}$$

, or a phenyl group, R_5, R_6, R_7 and R_8 each represent a hydrogen atom or an alkyl group having 1 to 18 carbon atoms.

The alkyl group represented by R_1, R_2, R_3, R_4, R_9 and R_{10} may be substituted or unsubstituted and may include, for example, a methyl group, an ethyl group, an iso-propyl group, an n-propyl group, a t-butyl group, a n-butyl group, a hydroxymethyl group, a hydroxyethyl group, a methylcarboxylic acid group, a benzyl group, etc. The alkyl group represented by R_5, R_6, R_7 and R_8 may also include those same as the above, and may additionally include an octyl group.

The phenyl group represented by R_1, R_2, R_3, R_4, R_9 and R_{10} may include a phenyl group, a 2-hydroxyphenyl group, a 4-aminophenyl group, etc.

Typical examples of the chelating agent of this invention are shown below, but by no means limited to these.

(II-1) 4-Isopropyl-1,2-dihydroxybenzene
(II-2) 1,2-Dihydroxybenzene-3,5-disulfonic acid
(II-3) 1,2,3-Trihydroxybenzene-5-carboxylic acid
(II-4) 1,2,3-Trihydroxybenzene-5-carboxymethyl ester
(II-5) 1,2,3-Trihydroxybenzene-5-carboxy-n-butyl ester
(II-6) 5-t-Butyl-1,2,3-trihydroxybenzene
(II-7) 1,2-Dihydroxybenzene-3,5,6-trisulfonic acid
(II-8) 1,2-Dihydroxybenzene-6-chloro-3,5-disulfonic acid
(II-9) 1,2-Dihydroxybenzene-3,4,5,6-tetrasulfonic acid
(III-1) 2,3-Dihydroxynaphthalene-6-sulfonic acid
(III-2) 2,3,8-Trihydroxynaphthalene-6-sulfonic acid
(III-3) 2,3-Dihydroxynaphthalene-6-carboxylic acid

(III-4) 2,3-Dihydroxy-8-isopropyl-naphthalene
(III-5) 2,3-Dihydroxy-8-chloro-naphthalene-6-sulfonic acid

Among the above compounds, particularly preferably used in this invention is 1,2-dihydroxybenzene-3,5-disulfonic acid, which may be also used as alkali salts such as a sodium salt and a potassium salt.

In this invention, the above chelating agent represented by General Formula (II) or (III) of this invention may be used in the range of 5 mg to 20 g, preferably added in an amount of 10 mg to 10 g, more preferably 20 mg to 3 g, per 1 liter of the developing solution, to obtain good results.

The chelating agent of this invention may be used alone or may be used in combination. There may be further used, in combination, other chelating agents such as aminopolyphosphonic acids such as aminotri(methylene-phosphonic acid) and ethylenediaminetetraphosphoric acid, oxycarboxylic acids such as citric acid and gluconic acid, phosphonocarboxylic acids such as 2-phosphonobutane-1,2,4-tricarboxylic acid, polyphosphoric acids such as tripolyphosphoric acid and hexametaphosphoric acid.

The color developing agent used in the color developing solution of this invention may preferably include p-phenylenediamine type compounds having a water soluble group.

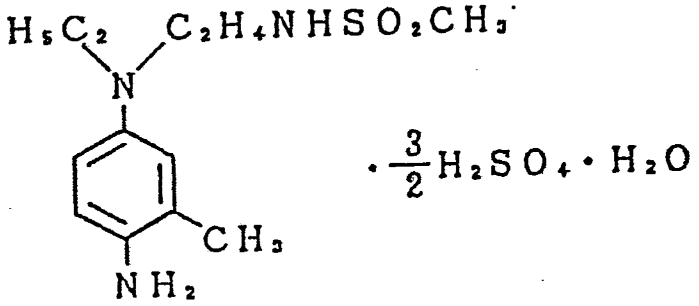
The p-phenylenediamine type compounds having a water soluble group have advantages not only that they may produce no stain on light-sensitive materials and hardly cause a rash on skin even if the skin was smeared with them, as compared with p-phenylenediamine type compounds having no water soluble group such as N,N-diethyl-p-phenylenediamine or the like, but also that they can afford to effectively achieve the objects of this invention by using them particularly in combination with the compound represented by General Formula (I) in this invention.

The above water soluble group may be such that at least one water soluble group is possessed on an amino group or benzene ring of the p-phenylenediamine type compounds. Specific water soluble group may preferably include $-(CH_2)_n-CH_2OH$, $-(CH_2)_mNHSO_2-(CH_2)_n-CH_3$, $-(CH_2)_mO-(CH_2)_n-CH_3$, $-(CH_2CH_2O)_nC_mH_{2m+1}$ (m and n each represent an integer of 0 or more), a -COOH group, a $-SO_3H$ group.

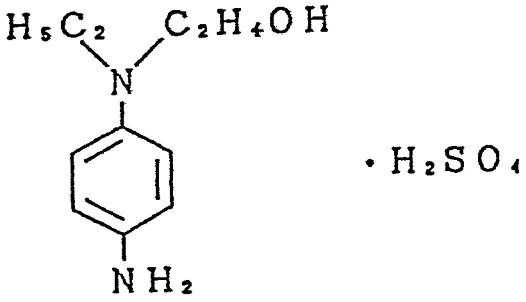
Specific exemplary compounds of the color developing agent preferably used in this invention are shown below.

Exemplary color developing agents

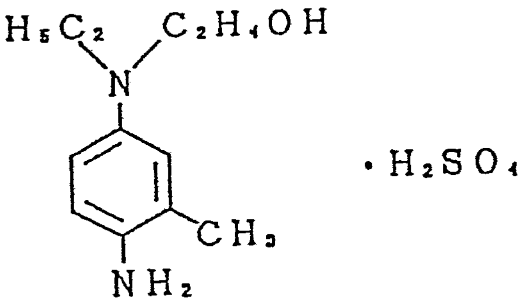
(A－1)


H₅C₂
C₂H₄NHSO₂CH₃
N
CH₃
NH₂
· 3/2 H₂SO₄ · H₂O

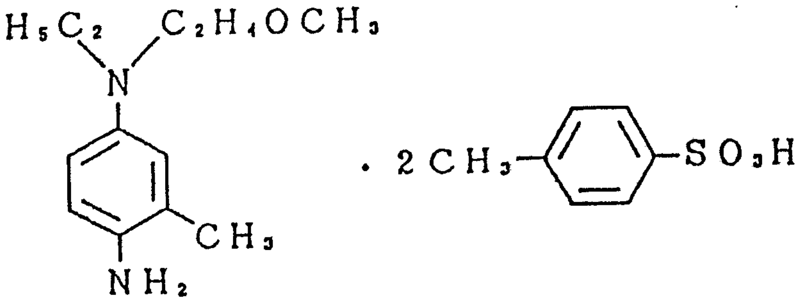
(A－2)


H₅C₂
C₂H₄OH
N
NH₂
· H₂SO₄

(A－3)


H₅C₂
C₂H₄OH
N
CH₃
NH₂
· H₂SO₄

(A－4)



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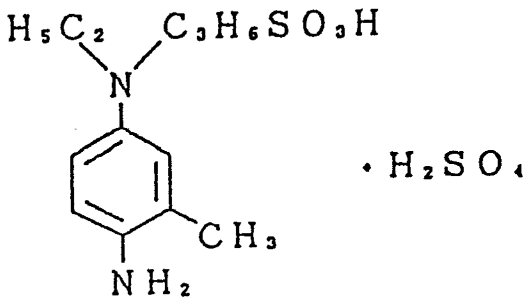

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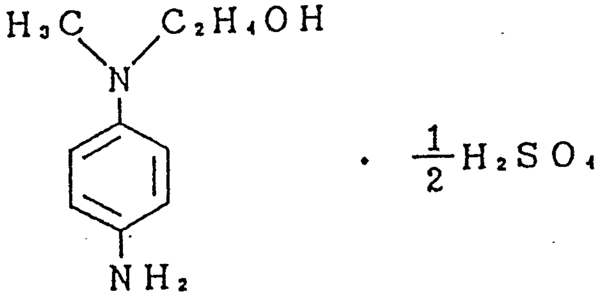

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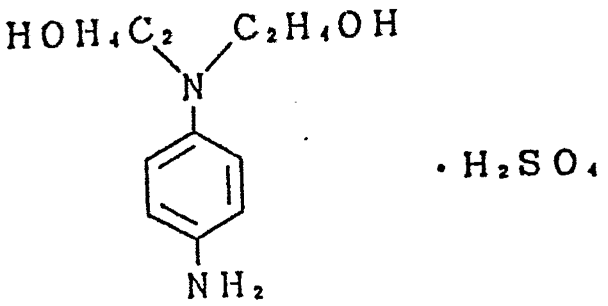
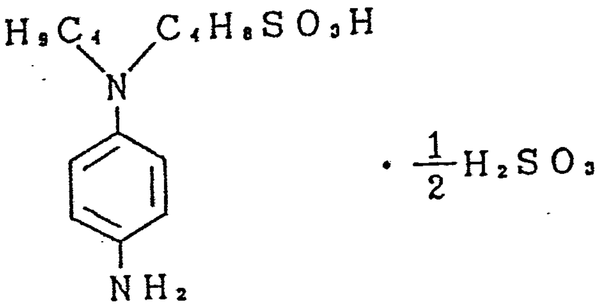
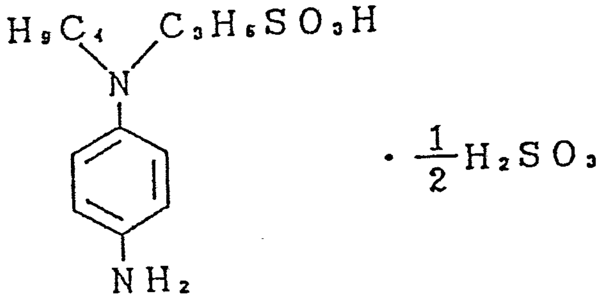

HOH₄C₂
C₂H₄OH
N
NH₂
· H₂SO₄

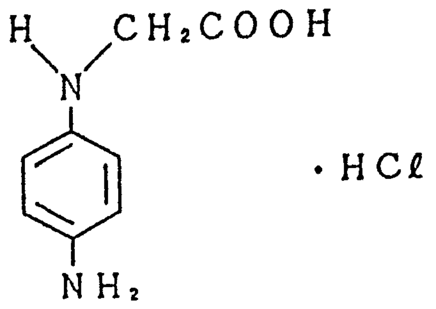
(A－8)


H₉C₄
C₄H₈SO₃H
N
NH₂
· ½H₂SO₃

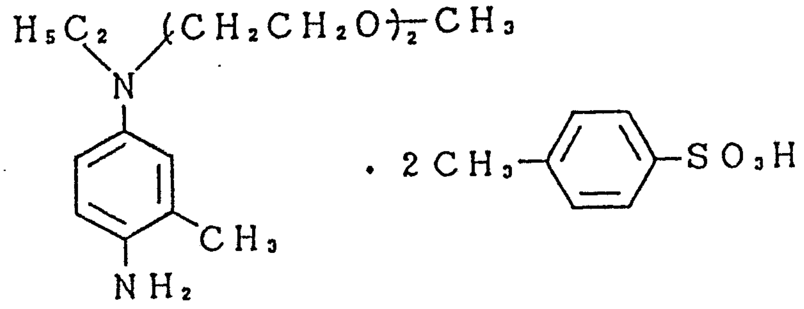
(A－9)


H₉C₄
C₃H₆SO₃H
N
NH₂
· ½H₂SO₃

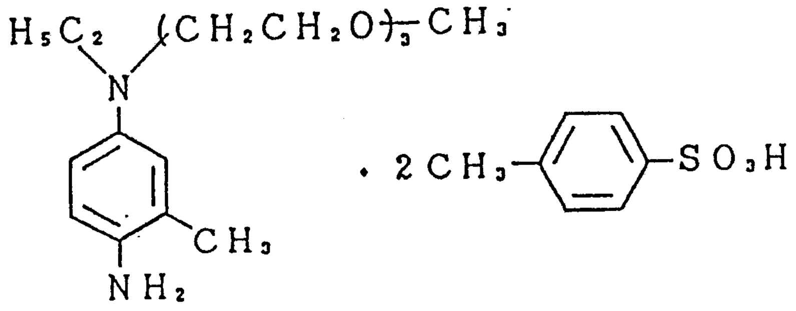
(A-10)



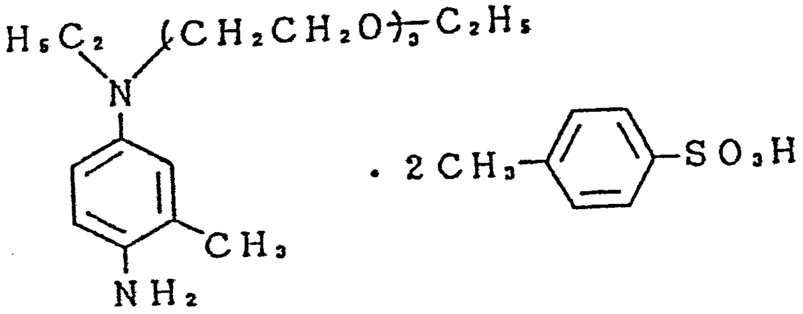
(A-11)



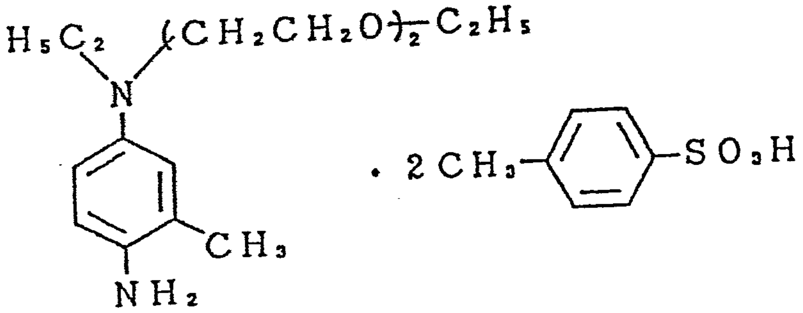
(A-12)



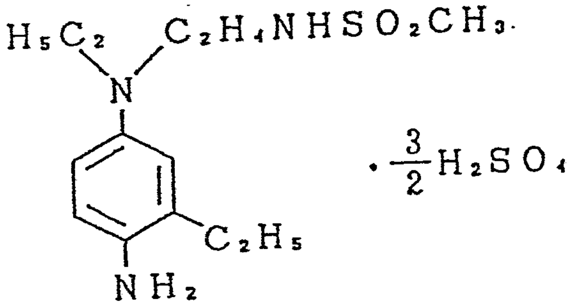
(A－13)


H₅C₂
(CH₂CH₂O)₃ C₂H₅
N
CH₃
NH₂
· 2CH₃
SO₃H

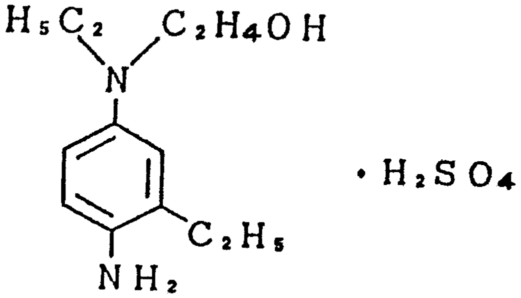
(A－14)


H₅C₂
(CH₂CH₂O)₂ C₂H₅
N
CH₃
NH₂
· 2CH₃
SO₃H

(A－15)


H₅C₂
C₂H₄NHSO₂CH₃
N
C₂H₅
NH₂
· 3/2 H₂SO₄

(A-16)



Among the color developing agents exemplified in the above, those which can be preferably used in this invention as being free from generation of fog are compounds shown as exemplary Nos. (A-1), (A-2), (A-3), (A-4), (A-6), (A-7) and (A-15), and particularly preferable compound is No. (A-1).

The above color developing agents are generally used in the form of salts such as hydrochloride, sulfate, p-toluenesulfonate, etc.

The color developing agent having a water soluble group, used in this invention, may be used preferably in the range of 1×10^{-2} to 2×10^{-1} mole per 1 liter of the color developing solution, more preferably from a viewpoint of the rapid processing, in the range of 1.5×10^{-2} to 2×10^{-1} mole per 1 liter of the color developing solution.

The color developing solution of this invention may contain the following developing solution components, in addition to the above component.

As alkali agents other than the above carbonates, sodium hydroxide, potassium hydroxide, silicate, sodium metaborate, potassium metaborate, trisodium phosphate, tripotassium phosphate, borax, etc. may be used alone or in combination so far as the above effects of this invention, namely, the effect of no occurrence of precipitation and the effect of making the pH stable can be maintained. If necessary for the preparation of the solution, or for the purpose of increasing intensity of ions, there can be used a variety of salts such as disodium hydrogenphosphate, dipotassium hydrogenphosphate, sodium bicarbonate, potassium bicarbonate and borate.

If necessary, an inorganic or organic antifoggant may be also added.

If necessary, a development accelerator can be also used. Such a developing accelerator may include every kind of pyridinium compounds as typified by those disclosed in U.S. Patents No. 2,648,604 and No. 3,671,247, and Japanese Patent Publication No. 9503/1969 and other cationic compounds, cationic dyes such as phenosafranine, neutral salts such as thallium nitrate, polyethylene glycol or derivatives thereof disclosed in U.S. Patents No. 2,533,990, No. 2,531,832, No. 2,950,970 and No. 2,577,127 and Japanese Patent Publication No. 9504/1969, nonionic compounds such as polythioethers, organic solvents disclosed in Japanese Patent Publication No. 9509/1969, or organic amines, ethanolamine, ethylenediamine, diethanolamine, triethanolamine, etc. It may also include benzyl alcohol disclosed in U.S. Patent No. 2,304,925, phenethyl alcohol, and besides these, acetylene glycol, methyl ethyl ketone, cyclohexane, thioethers, pyridine, ammonia, hydrazine, amines, etc.

In the above, the bad soluble organic solvent particularly typified by benzyl alcohol tends to cause appearance of tar after use of the color developing solution for a long period of time, particularly during the running processing according to a low replenishing system. Appearance of such tar, when adhered on a paper light-sensitive material to be processed, may even bring about such a serious trouble that a commercial value of the product is extremely damaged.

Also, since the bad solvent organic solvent has poor solvency to water, there is not only a cumbersomeness that a stirring instrument is needed to prepare the color developing solution itself, but also a limit to the development accelerating effect due to the badness of its solvency rate even with use of such a stirring instrument.

The bad solvent organic solvent does further have problems such that it has a great value for the burden to environmental pollution such as biochemical oxygen demand (BOD), and cannot be abandoned in sewerages, rivers or the like, so that much labor and cost are needed for waste liquor disposal. Accordingly, it is preferably used in a decreased amount, or not used.

Further, in the color developing solution of this invention, if necessary, ethylene glycol, methyl cellosolve, methanol, acetone, dimethylformamide, β-cyclodextrin and other compounds disclosed in Japanese Paent Publications No. 33378/1972 and No. 9509/1969 can be used as an organic solvent for increasing the dissolving degree of a developing agent.

An auxiliary developing agent can be also used together with the developing agent. Such an auxiliary developing agent is known to include, for example, N-methyl-p-aminophenol hexasulfate (Metol), phenidone, N,N'-diethyl-p-aminophenol hydrochloride, N,N,N'N'-tetramethyl-p-phenylenediamine hydrochloride, and may be added usually in an amount of 0.01 g to 1.0 g/lit. Besides these, if necessary, there can be further added competing couplers, fogging agents, colored couplers, development restrainer-releasing type couplers (the so-called DIR couplers) or development restrainer-releasing compounds.

Still further, besides, various additives such as anti-stain agents, sludge preventive agents and interlayer effect accelerators can be used.

The respective components of the above color developing agent can be prepared by successively adding them to a given amount of water, followed by stirring. In this occasion, a component having poor solvency to water may be added by mixing it with the above organic solvent such as triethanolamine. More generally, a mixture of a plurality of components that can be stably present together with each other, prepared in the form of a concentrated aqueous solution or a solid in a small container, may be added in water and stirred to obtain a solution as the color developing solution of this invention.

In this invention, the above color developing agent can be used in a desired pH range, but, from a viewpoint of rapid processing, preferably in the range of pH 9.5 to 13.0, more preferably pH 9.8 to 13.0.

In this invention, the color developing processing temperature may be not lower than 30°C and not higher than 50°C, within which the higher it is, the more preferably it becomes possible to carry out rapid processing in a short time, but, from a viewpoint of image preservation stability, the temperature should not be so high. Thus, the processing is preferably carried out at not lower than 33°C and not higher than 45°C.

In general, the color developing is conventionally carried out in about 3 minutes and 30 seconds, but, in the present invention, it can be carried out in 2 minutes or less, or can be also carried out in the range of 30 seconds to 1 minute and 30 seconds.

This invention can be applied in any system if it is a system using the color developing solution containing the compound represented by the above General Formula (I) and at least one compound selected from the compound represented by the above General Formula (II) and the compound represented by the above General Formula

(III). For example, there can be used a monobath processing system, as well as other various types of processing systems such as a spray system in which a processing solution is formed into a spray, a web system utilizing the contact with a carrier impregnated with a processing solution, or a developing system using a viscous processing solution. However, the processing step should substantially comprise the steps of color developing, bleach-fixing and washing or stabilizing that can be substituted with the washing.

The bleach-fixing step may be constituted separately of a bleaching step and a fixing step, or may comprise a bleach-fixing bath carrying out the bleaching and fixing in a bath.

Bleaching agents that can be used in the bleach-fixing solution used in this invention are metal complex salts of organic acids. The complex salts are compounds formed by coordination of a metal ion such as iron, cobalt, copper, etc. with an organic acid such as aminopolycarboxylic acid or oxalic acid and citric acid. Most preferable organic acid used for the formation of metal complex salts may include polycarboxylic acid. These polycarboxylic acid and aminopolycarboxylic acid may be alkali metal salts, ammonium salts or water soluble amine salts. Specific examples of these may include the following:

[1] Ethylenediaminetetraacetic acid
[2] Diethylenetriaminepentaacetic acid
[3] Ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetic acid
[4] Propoylenediaminetetraacetic acid
[5] Nitrilotriacetic acid
[6] Cyclohexanediaminetetraacetic acid
[7] Iminodiacetic acid
[8] Dihydroxyethylglycinecitric acid (or tartaric acid)
[9] Ethyl ether diaminetetraacetic acid

[10] Glycol ether diaminetetraacetic acid
[11] Ethylenediaminetetrapropionic acid
[12] Phenylenediaminetetraacetic acid
[13] Ethylenediaminetetraacetic acid disodium salt
[14] Ethylenediaminetetraacetic acid tetra(trimethylammonium)salt
[15] Ethylenediaminetetraacetic acid tetrasodium salt
[16] Diethylenetriaminepentaacetic acid pentasodium salt
[17] Ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetic acid sodium salt
[18] Propylenediaminetetraacetic acid sodium salt
[19] Nitrilotriacetic acid sodium salt
[20] Cyclohexanediaminetetraacetic acid sodium salt

These bleaching agent may be used preferably in an amount of 5 to 450 g/lit., more preferably 20 to 250 g/lit. The bleach-fixing solution may contain a silver halide fixing agent in addition to the bleaching agent mentioned above, and, if necessary, a solution of the composition containing sulfite as a preservative may be used. There can be also used a bleach-fixing solution of the composition to which an ethylenediaminetetraacetic acid iron (III) complex salt bleaching agent and a halide such as ammonium bromide other than the above silver halide fixing agent are added in a small amount, or, on the contrary, a bleach-fixing solution of the composition to which a silver halide such as ammonium bromide is added in a large amount, or a special bleach-fixing solution of the composition comprising a combination of an ethylenediaminetetraacetic acid iron (III) complex salt bleaching agent and a large amount of silver halide such as ammonium bromide. The above halide that can be used may include, besides ammonium bromide, hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, potassium bromide, sodium iodide, potassium iodide, ammonium iodide, etc.

The silver halide fixing agent contained in the bleach-fixing solution may typically include the compounds capable of forming a water soluble complex salt by reacting with a silver halide, as used in ordinary fixing processing, for example, thiosulfates such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate; thiocyanates such as potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate; thioureas; thioethers; etc. These fixing agents may be used in an amount of 5 g/lit. or more and in the range of the amount that can be dissolved, and, in general, may be used in an amount of 70 g to 250 g/lit.

The bleach-fixing solution may contain, solely or in combination, a variety of pH buffering agents such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide. It may also contain various brightening agents, anti-foaming agents or surface active agents. It may further appropriately contain preservatives such as bisulfite addition products of hydroxylamine, hydrazine or an aldehyde compound, organic chelating agents such as aminopolycarboxylic acid or stabilizers such as nitroalcohol and nitrate, and organic solvents such as methanol, dimethylsulfonamide and dimethylsulfoxide.

To the bleach-fixing solution used in this invention, various bleach accelerating agents may be added, disclosed in Japanese Unexamined Patent Publication No. 280/1971, Japanese Patent Publications No. 8506/1970, and No. 556/1971, Belgian Patent No. 770,910, Japanese Patent Publications No. 8836/1970 and No. 9854/1978, Japanese Unexamined Patent Publications No. 71634/1979 and No. 42349/1974, etc. can be added.

The bleach-fixing solution may be used at the pH of 4.0 or more, but, in general, at the pH of not less than 5.0 and not more than 9.5, more preferably at the pH of not less than 6.0 and not more than 8.5, and still more preferably at the pH of not less than 6.5 and not more than 8.5 to carry out the processing. The processing temperature to be used may be a temperature of not less than 3°C, preferably not less than 5°C, lower than the processing temperature in a color developing tank, and, desirably, a temperature of not less than 55°C while suppressing the evaporation or the like.

In this invention, the above color developing and bleach-fixing steps are followed by washing or a process by use of washing solution substitute, so-called washing substitutive stabilizing processing, in place of the washing.

The process of the water washing substitute according to this invention is a process carried out in place of a water washing step following on a fixing step or a bleach-fixing step. Conventional water washing process is a process for washing away, by washing with water, a processing solution of a previous bath contained in structural layers of the light-sensitive material, specifically a large amount of thiosulfates, chemicals and silver complex salts contained in a fixing solution or a bleach-fixing soluiton, chemicals contained in a color developing solution and the like. This process includes, for example, a method in which a large amount of flowing water is flown on the surface of a light-sensitive material in a water washing bath to remove the processing solution of the provious bath, a substituting water washing method in which a light-sensitive material is dipped in a constant amount of water and the water is changed by fresh water after constant time passed, etc. Although, this water washing process is usually carried out only by use of water, it may be conducted after dipping the light-sensitive material in a bath containing salts such as sodium sulfite, etc. for several minutes in order to accelerate the processing speed. In any event, the water processing is carried out by using water. Therefore, a large amount of water for washing is required for preventing any troubles such as drying of the light-sensitive material, dirt, discoloration and fading of images, etc. during storage caused by chemicals such as thiosulfate remained in the light-sensitive material. Further, since equipments for discharging the water is required after the water washing process, such process is not good spatially and economically. The process by use of the washing solution substitute dissolved such problems. The processing solution used for the process is not merely water, but a solution containing an antimildew, antiseptic, disinfection means, further optionally, a chelating agent having the chelating stabilization degree against ferric ion of 8 or more, ammonia compounds, organic acid salts, pH adjusting agents, surfactants, sulfites, brightening agents, etc.

In the conventional water washing process, the compounds adhered or permeated in the light-sensitive material such as thiosulfates, etc. were washed away by replenishing water in about 5 lit. to 150 lit. per 1 m^2 of the light-sensitive material. On the other hand, according to the process of washing solution substitute of this invention, such compounds adhered or permeated in the light-sensitive material is washed away by a replenished amount of about 0.01 lit. to 2.5 lit. per 1 m^2 of the light-sensitive material. Further, since the process of this invnetion can be made by use of very little replenished amount as compared with the convnetional processes, feeding- and discharging-piping equipments of water to an automatic processing machine which has been required in the conventional water washing process became not to be necessarily required, and thus miniturization of the equipment is accomplished.

The processing by use of washing solution substitute applicable in this invention will be described below.

The pH of the washing soluiton substitute may range between 5.5 and 10.0. The pH-adjusting agents that can be contained in the washing solution substitute applicable in this invention may be any of those of alkali agents or acid agents generally known in the art.

The processing by use of the washing solution substitute (or the stabilizing processing or steps) may be carried out at a temperature ranging between 15°C and 60°C, preferably 20°C and 45°C. The processing time as short as possible is also more preferable from a viewpoint of the rapid processing, but, in general, may be in the range of 20 seconds to 10 minutes, most preferably 1 minute to 3 minutes. In the case of the processing of washing solution substitute using multiple tanks, it is also preferable to carry out the processing in a shorter time in anterior tanks and in a longer time in posterior tanks. It is particularly preferable to successively carry out the processing in such a time that is 20 % to 50 % longer than the processing time in an anterior tank. No washing is required at all after the processing of washing solution substitute applicable in this invention, but rinsing with use of small amount of water in a very short time or surface washing may be optionally carried out if necessary.

The processing of washing solution substitute (or the stabilizing step) applicable in this invention may be supplied, in the case of a multiple tank counter current system, in such a manner that the solution is supplied to a posterior tank and overflowed from an anterior tank. As a matter of course, the processing may be carried out in a single tank. As the method of adding above compounds, various methods are available, including a method in which the compounds are added to a stabilizing tank in the form of a concentrated solution, or a method in which the above compounds and other additives are added to the washing soluiton substitute supplied to a stabilizing tank, and the resulting solution is used as a supplying solution for replenishing the washing solution substitute. Any of these method may be used for the addition.

Thus, in this invention, the processing by the washing soluiton substitute also refers to the processing for stabilizing, wherein stabilizing processing is carried out immediately after processing by a processing solution having bleach-fixing ability without substantially carrying out washing with water, and the processing solution used in such stabilizing solution is called the washing solution substitute, and the processing tank is called a washing solution substitute tank (or a stabilizing bath or a stabilizing tank).

The stabilizing tank in the stabilizing processing applicable in this invention may preferably comprise 1 to 5 tanks, particularly preferably 1 to 3 tanks, and not more than 9 tanks at most.

According to the preferred embodiment of the present invention, the method of processing the light-sensitive silver halide color photographic material of this invention is to process a light-sensitive silver halide color photographic material having a silver halide emulsion layer containing silver halide grains substantially comprised of silver chloride, by using the aforesaid color developing solution used in this invention, i.e., the color developing solution containing as preservatives the compounds of this invention, the compound (I).

The silver halide grains used in the light-sensitive silver halide color photographic material applied in this invention are preferably substantially comprised of silver chloride. In this invention, the terms "silver halide grains substantially comprised of silver chloride" are meant to be silver halide grains containing at least not less than 80 mole %, preferably not less than 90 mole %, and more preferably not less than 95 mole %, of silver chloride.

The silver halide emulsion containing the above silver halide grains substantially comprised of silver chloride may contain, besides silver chloride, silver bromide and/or silver iodide as the silver halide composition. In such a case, silver bromide may be contained in an amount of 20 mole % or less, preferably 10 mole % or less, more preferably 5 mole % or less. When silver iodide is present, it may be contained in an amount of 1 mole % or less, preferably 0.5 mole % or less. Such silver halide grains of this invention, substantially comprised of silver chloride may be contained preferably to account for 80 % or more, more preferably 100 %, in % by weight, of total silver halide grains in the silver halide emulsion layers which contain the silver halide grains.

Crystals of the silver halide grains used in this invention may be of regular crystals, twin crystals or others, and there can be used those having any ratio of [100] face to [111] face. The crystal structure of these silver halide grains may be uniform through inside to outside, or may be of layered structure comprising an inside and outside of different nature (a core/shell type). These silver halide grains may be also of the type such that a latent image is chiefly formed on the surface, or of the type wherein it is formed in the inside of a grain. Tabular silver halide grains (see Japanese Unexamined Patent Publication No. 113934/1983 and Japanese Patent Application No. 170070/1984) can be also used.

The silver halide grains used in this invention may be obtained by any preparation methods including an acidic method, a neutral method and an ammoniacal method.

Alternatively, seed grains may be prepared according to an acidic method, which are allowed to grow according to an ammoniacal method that can achieve higher growth rate, until they grow to have given size. When growing the silver halide grains, it is preferable to control the pH and pAg in a reaction vessel, and pouring and mixing silver ions and halide ions successively and simultaneously in the amount corresponding to the growth rate of silver halide grains as disclosed, for example, in Japanese Unexamined Patent Publication No. 48521/1979.

The silver halide grains according to this invention are preferably prepared in the above-mentioned manner. In the present specification, a composition containing such silver halide grains are referred to as a silver halide emulsion.

The silver halide emulsion may be chemically sensitized by using active gelatin; sulfur sensitizing agents, for example, sulfur sensitizing agents such as allylthiocarbamide, thiourea and cystine; selenium sensitizing agents; reduction sensitizing agents, for example, stunnous salts, thiourea dioxide, polyamine, etc.; noble metal sensitizing agents, for example, gold sensitizing agents, specifically including sensitizing agents such as potassium aurothiocyanate, potassium chloroaurate and 2-aurothio-3-methylbenzothiazolium chloride, or sensitizing agents having a water soluble group, for example, ruthenium, palladium, platinum, rhodium, iridium, etc., specifically including ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladate (Some of their act as a sensitizing agent or a fog-suppressing agent depends on whether they are in a large amount or a small amount.), etc., which may be used alone or in appropriate combination (for example, combination of a gold sensitizing agent with a sulfur sensitizing agent, combination of a gold sensitizing agent with a selenium sensitizing agent, etc.).

The silver halide emulsion according to this invention may be subjected to chemical ripening by adding a sulfur-containing compound, and, before such chemical ripening, during the ripening, or after the ripening, at least one of hydroxytetrazaindenes and at least one of nitrogen-containing heterocyclic compounds having a mercapto group may be contained.

The silver halide used in this invention may be optically sensitized by adding a suitable sensitizing dye in amount of 5×10^{-8} mole to 3×10^{-3} mole per mole of silver halide so that sensitivities to respectively desired light-sensitive wavelength regions can be imparted thereto. There can be various types of sensitizing dyes, which sensitizing dyes can be used alone or in combination with two or more of them. The sensitizing dyes advantageously used in this invention may include, for example, the following:

Sensitizing dyes to be used in a blue-sensitive silver halide emulsion may include, 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, British Patent No. 1,242,588, Japanese Patent Publications No. 14033/1969 and No. 24844/1977, etc. Sensitizing dyes to be used in a green-sensitive silver halide emulsion may typically include, 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, British Patent No. 505,979, etc. Further, sensitizing dyes to be used in a red-sensitive silver halide emulsion may typically include, 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, etc.

Still further, the cyanine dyes, merocyanine dyes or composite cyanine dyes as disclosed in U.S. Patents No. 2,213,995, No. 2,493,748 and No. 2,519,001, West German Patent No. 929,080 can be advantageously used in the green-sensitive silver halide emulsion or the red-sensitive silver halide emulsion.

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

If necessary, the light-sensitive photographic material of this invention may be optically sensitized to a desired wavelength region according to a spectral sensitization method by using a cyanine dye or a merocyanine dye alone or in combination.

A particularly preferable spectral sensitization method may typically include the methods disclosed in Japanese Patent Publications No. 4936/1968, No. 22884/1968, No. 18433/1970, No. 37443/1972, No. 28293/1973, No. 6209/1974 and 12375/1978, Japanese Unexamined Patent Publications No. 23931/1977, No. 51932/1977, No. 80118/1979, No. 153926/1983, No. 116646/1984 and No. 116647/1984, etc., which are concerned with the combination of benzimidazolocarbocyanine with benzoxazolocarbocyanine.

Those concerned with the combination of carbocyanine having a benzimidazole nucleus with other cyanines or merocyanines may include, 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, 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, etc.

Those concerned with the combination of benzoxazolocarbocyanine (oxa•carbocyanine) with other carbocyanines may include, for example, those disclosed in Japanese Patent Publications No. 32753/1969 and No.

11627/1971, Japanese Unexamined Patent Publication No. 1483/1982, etc., and those concerned with merocyanine may include, for example, those disclosed in Japanese Patent Publications No. 38408/1973, No. 41204/1973 and No. 40662/1975, Japanese Unexamined Patent Publications No. 25728/1981, No. 10753/1983, No. 91445/1983, No. 116645/1984 and No. 33828/1975, etc.

Also, the methods concerned with the combination of thiacarbocyanine with other carbocyanines may include, for example, those disclosed in Japanese Patent Publications No. 4932/1968, No. 4933/1968, No. 26470/1970, No. 18107/1971 and NO. 8741/1972, Japanese Unexamined Patent Publication No. 114533/1984, etc., and the methods disclosed in Japanese Patent Publication No. 6207/1974, employing zeromethine- or dimethine-merocyanine, monomethine- or trimethinecyanine and styryl dyes, can be advantageously used.

In adding these sensitizing dyes to the silver halide emulsion according to this invention, they are used as a dye solution obtained by previously dissolving them in a hydrophilic organic solvent such as methyl alcohol, ethyl alcohol, acetone, dimethylformamide and fluorinated alcohol disclosed in Japanese Patent Publication No. 40659/1975.

They may be added at any time at the initiation of chemical ripening of the silver halide emulsions, during the ripening, or after completion of the ripening, or in some cases, at the step right before the coating of the emulsion.

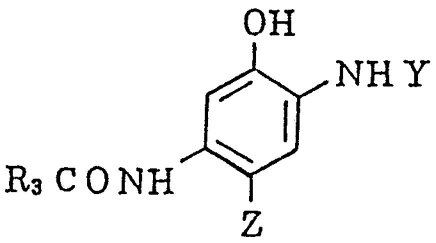
Dyes that are water soluble or decolored by a color developing solution (AI dyes) may be added to photographic constituent layers of the light-sensitive silver halide color photographic material of this invention. The AI dyes may include oxonol dyes, hemioxonol dyes, merocyanine dyes and azo dyes. Among them, particularly useful are oxonol dyes, hemioxonol dyes and merocyanine dyes. Examples of the AI dyes may include those disclosed in British 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, No. 4,071,312 and No. 4,070,352.

In general, these AI dyes may be used preferably in an amount of 2×10^{-3} to 5×10^{-1} mole, more preferably 1×10^{-2} to 1×10^{-1} mole, per mole of silver in an emulsion layer.

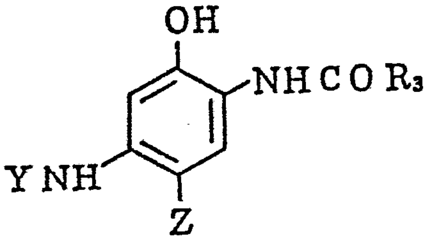
According to the another preferred embodiment of this invention, the processing method of the light-sensitive silver halide color photographic material of this invention is carried out by processing the light-sensitive silver halide material containing at least one selected from cyan couplers of (C - I), (C - II) and (C - III) in at least one silver halide emulsion layer, by use of the color developing solution of this invention containing the compound of formula (I) as a preservative and the compound of formula (II) or (III) as a chelating agent.

Hereinafter, the cyan coupler represented formula (C - I) or (C - II) will be described.

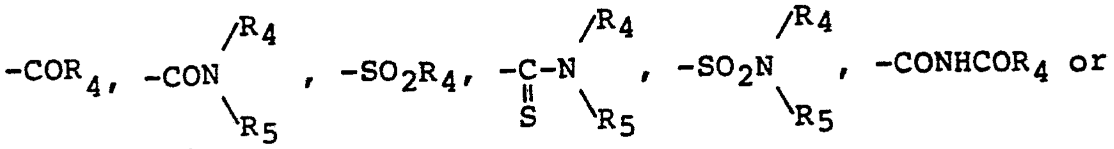
Formula (C-I)



Formula (C-II)



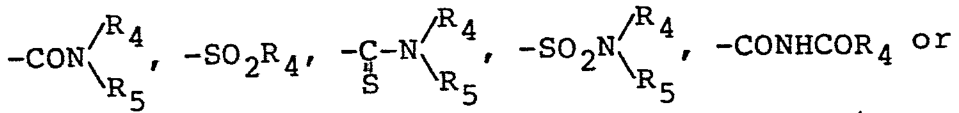
In formulae (C - I) and (C - II), Y represents



$-\mathrm{COR}_4$, $-\mathrm{CON}<^{R_4}_{R_5}$, $-\mathrm{SO_2R_4}$, $-\underset{\overset{\|}{S}}{\mathrm{C}}-\mathrm{N}<^{R_4}_{R_5}$, $-\mathrm{SO_2N}<^{R_4}_{R_5}$, $-\mathrm{CONHCOR}_4$ or $-\mathrm{CONHSO_2R_4}$

(where R_4 represents an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or a heterocyclic group; R_5 represents a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or a heterocyclic group; and R_4 and R_5 may be bonded with each other to form a 5- or 6-membered ring); R_3 represents a ballast group; and Z represents a hydrogen atom or a group eliminatable through the coupling reaction with the oxidized product of an aromatic primary amine series color developing agent.

Next, the cyan coupler represented by the formulae (C - I) or (C -II) to be used in the present invention will be explained. In the above formulae (C - I)) and (C - II)), Y is a group represented by $-\mathrm{COR}_4$,



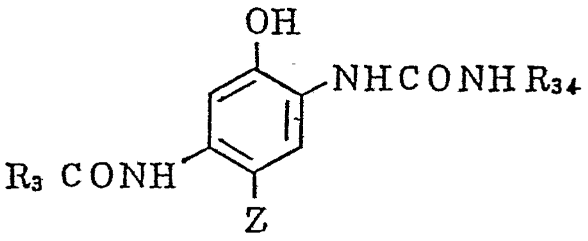
$-\mathrm{CON}<^{R_4}_{R_5}$, $-\mathrm{SO_2R_4}$, $-\underset{\overset{\|}{S}}{\mathrm{C}}-\mathrm{N}<^{R_4}_{R_5}$, $-\mathrm{SO_2N}<^{R_4}_{R_5}$, $-\mathrm{CONHCOR}_4$ or

$-\mathrm{CONHSO_2R_4}$. In these formulae, R_4 represents an alkyl group, preferably an alkyl group having 1 to 20 carbon atoms (e.g. a methyl group, an ethyl group, a t-butyl group, a dodecyl group, etc.), an alkenyl group, preferably an alkenyl group having 2 to 20 carbon atoms (e.g. an allyl group, a heptadecenyl group, etc.), a cycloalkyl group, preferably that of 5 to 7-membered ring (e.g. a cyclohexyl group, etc.), an aryl group (e.g. a phenyl group, a tolyl group, a naphthyl group, etc.), or a heterocyclic group, preferably a 5-membered or 6-membered heterocyclic ring containing 1 to 4 nitrogen atoms, oxygen atoms or sulfur atoms (e.g. a furyl group, a thienyl group, a benzothiazolyl group, etc.). R_5 represents a hydrogen atom or a group represented by R_4. R_4 and R_5 may be bound to each other to form a 5- or 6-membered heterocyclic ring containing a nitrogen atom. R_4 and R_5 may optionally have a substituent or substituents including, for example, an alkyl group having 1 to 10 carbon atom (e.g. ethyl, i-propyl, i-buytl, t-butyl, t-oxtyl, etc.), an aryl group (e.g. phenyl, naphthyl, etc.), a halogen atom (fluorine, chlorine, bromine, etc.), a cyano group, a nitro group, a sulfonamido group (e.g. methansulfonamido, butansulfonamido, p-toluenesulfonamido, etc.), a sulfamoyl group (e.g. methylsulfamoyl, phenylsulfamoyl, etc.), a sulfonyl group (e.g. methansulfonyl, p-toluenesulfonyl, etc.), a fluorosulfonyl group, a carbamoyl group (e.g. dimethylcarbamoyl, phenylcarbamoyl, etc.), an oxycarbonyl group (e.g. ethoxycarbonyl, phenoxycarbonyl, etc.), an acyl group (e.g. acetyl, benzoyl, etc.), a heterocyclic group (e.g. a pyridyl group, a pyrazolyl group, etc.), an alkoxy group, an aryloxy group, an acyloxy group and the like.

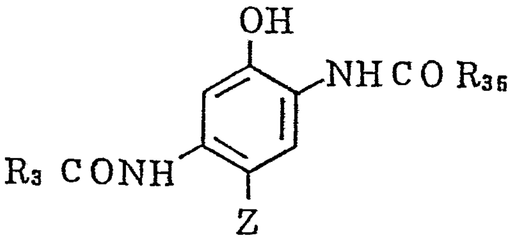
In formulae (C - I) and (C - II), R_3 represents a ballast group necessary for providing a diffusion resistance to the cyan coupler represented by formulae (C - I) and (C - II)) and a cyan dye derived from said cyan coupler. Preferably, R_3 may be an alkyl group having 4 to 30 carbon atoms, an aryl group or a heterocyclic group. For example, R_3 may include a straight or branched alkyl group (e.g. t-butyl, n-octyl, t-octyl, n-dodecyl, etc.), an alkenyl group, a cycloalkyl group, a 5-membered or 6-membered heterocyclic group and the like.

In formulae (C - I) and (C - II), Z represents a hydrogen atom or a group eliminatable through the coupling reaction with an oxidized product of color developing agent. For example, z may include a halogen atom (e.g. chlorine, bromine, fluorine, etc.), a substituted or unsubstituted alkoxy, aryloxy, heterocyclyloxy, acyloxy, carbamoyloxy, sulfonyloxy, alkylthio, arylthio, heterocyclicthio or sulfonamido group, etc. and more specifically, those as 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 Nos. 10135/1975, 117422/1975, 130441/1975, 108841/1976, 120343/1975, 18315/1977, 105226/1978, 14736/1979, 48237/1979, 32071/1980, 65957/1980, 1938/1981, 12643/1981, 27147/1981, 146050/1984, 166956/1984, 24547/1985, 35731/1985 and 37557/1985.

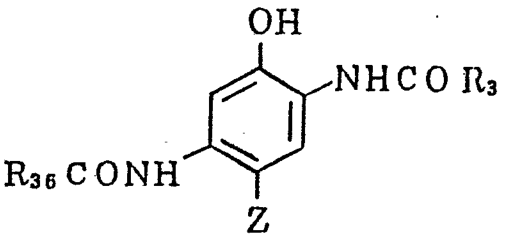
In the present invention, of the cyan couplers represented by the above formulae (C - I) or (C - II), the cyan couplers represented by the following formula (C - IV), (C - V) or (C - VI) are more preferred.



(C - IV)

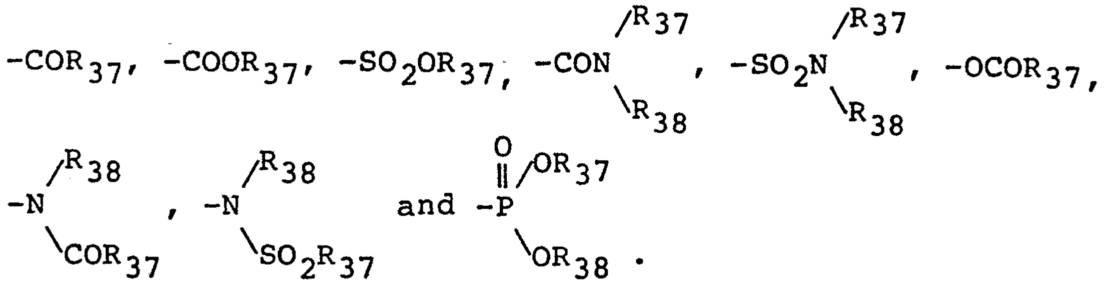


(C - V)



(C - VI)

In formula (C - IV), R_{34} is a substituted or unsubstituted aryl group (particularly preferred is a phenyl group). As the substituent for said aryl group represented by R_{34}, they may be mentioned at least one substituent selected from $-SO_2R_{37}$, a halogen atom (e.g. fluorine, bromine, chlorine, etc.), $-CF_3$, $-NO_2$, $-CN$,



$-COR_{37}$, $-COOR_{37}$, $-SO_2OR_{37}$, $-CON\begin{smallmatrix}R_{37}\\R_{38}\end{smallmatrix}$, $-SO_2N\begin{smallmatrix}R_{37}\\R_{38}\end{smallmatrix}$, $-OCOR_{37}$,

$-N\begin{smallmatrix}R_{38}\\COR_{37}\end{smallmatrix}$, $-N\begin{smallmatrix}R_{38}\\SO_2R_{37}\end{smallmatrix}$ and $-\overset{O}{\overset{\|}{P}}\begin{smallmatrix}OR_{37}\\OR_{38}\end{smallmatrix}$.

In the above, R_{16} represents an alkyl group, preferably an alkyl group having 1 to 20 carbon atoms (e.g. methyl, ethyl, tert-butyl, dodecyl, etc.), an alkenyl group, preferably an alkenyl group having 2 to 20 carbon atoms (e.g. an allyl group, a heptadecenyl group, etc.), a cycloalkyl group, preferably 5 to 7-membered ring group (e.g. a cyclohexyl group, etc.), an aryl group (e.g. a phenyl group, a tolyl group, a naphthyl group, etc.); and R_{38} is a hydrogen atom or a group represented by the above R_{37}.

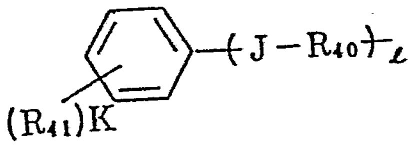
The preferred compounds of the phenol type cyan coupler represented by (C - IV) includes a compound in which R_{37} is a substituted or unsubstituted phenyl group, and the substituent for the phenyl group includes a cyano group, a nitro group, $-SO_2R_{39}$ (in which R_{39} is an alkyl group), a halogen atom or a trifluoromethyl group.

In the formulae (C - V) and (C - VI), R_{35} and R_{36}

each represent an alkyl group, preferably an alkyl group having 1 to 20 carbon atoms (e.g. methyl, ethyl, tert-butyl, dodecyl, etc.), an alkenyl group, preferably an alkenyl group having 2 to 20 carbon atoms (e.g. allyl, oleyl, etc.), a cycloalkyl group, preferably a 5- to 7-membered cyclic group (e.g. cyclohexyl, etc.), an aryl group (e.g. a phenyl group, a tolyl group, a naphthyl group, etc.), a heterocyclic group (preferably a hetero ring of 5-membered or 6-membered hetero ring having 1 to 4 atoms of a nitrogen atom, an oxygen atom or a sulfur atom, such as a furyl group, a thienyl group, a benzothiazolyl group, etc.) and the like.

In the aforesaid R_{37} and R_{38}, and R_{35} and R_{36} of formulae (C - V) and (C - VI), optional substituents may be introduced therein, and such substituents may be those which may be introduced in R_4 or R_5 in formulae (C - I) and (C - II) as mentioned above. As the substituent, a halogen atom (a chlorine atom, a fluorine atom, etc.) is particularly preferred.

In the above formulae (C - IV), (C - V) and (C - VI), Z and R_3 each have the same meanings as in formulae (C - I) and (C - II). Preferred examples of the ballast group represented by R_3 is a group represented by the following formula (C - VII):

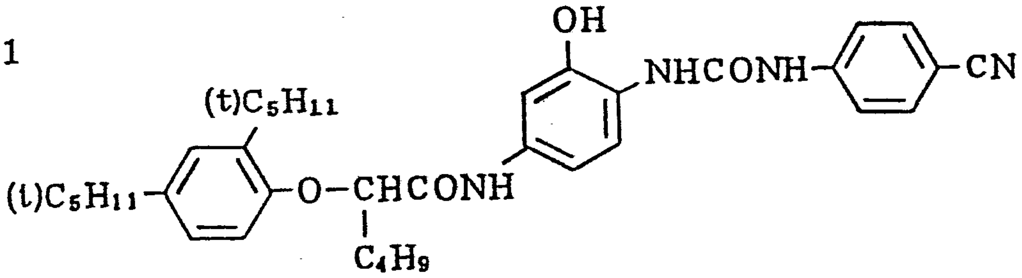


(C - VII)

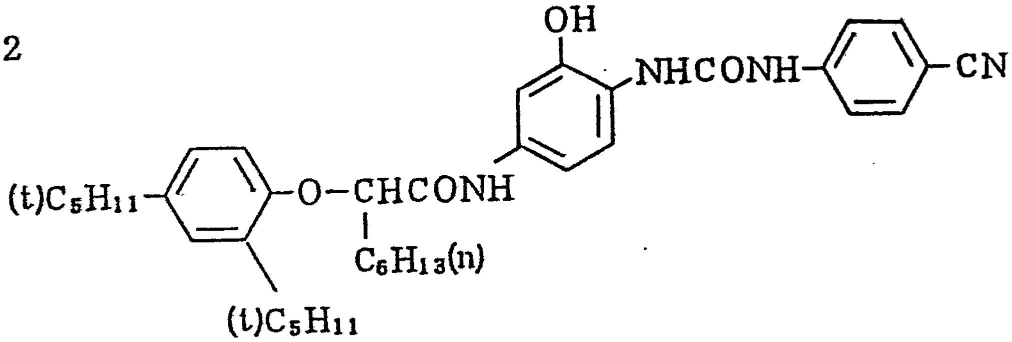
In Formula (C - VII), J represents an oxygen atom, a sulfur atom or a sulfonyl group; k represents an integer of 0 to 4; ℓ represents 0 or 1; provided that when k is 2 or more, 2 or more of R_{41} may be the same or different from each other; R_{40} represents a straight or branched alkylene group having 1 to 20 carbon atoms which may be substituted by an aryl group, etc.; R_{41} represents a monovalent group, preferably a hydrogen atom, a halogen atom (e.g. chlorine, bromine, etc.), an alkyl group, preferably a straight or branched alkyl group having 1 to 20 carbon atoms (e.g. methyl, t-butyl, t-pentyl, t-octyl, dodecyl, pentadecyl, benzyl, phenethyl, etc.), an aryl group (e.g. a phenyl group), a heterocyclic group (preferably a nitrogen containing heterocyclic group), an alkoxy group, preferably a straight or branched alkoxy group having 1 to 20 carbon atoms (e.g. methoxy, ethoxy, t-butyloxy, octyloxy, decyloxy, dodecyloxy, etc.), 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, a benzoyloxy group), a carboxy group, an alkyloxycarbonyl group, preferably a straight or branched alkyloxycarbonyl group having 1 to 20 carbon atoms, an aryloxycarbonyl group, preferably a phenoxycarbonyl group, an alkylthio group preferably having 1 to 20 carbon atoms, an acyl group, a straight or branched alkylcarbonyl group which may preferably have 1 to 20 carbon atoms, an acylamino group, a straight or branched alkylcarboamide group which may preferably have 1 to 20 carbon atoms, a benzenecarboamido group, a sulfonamido group, preferably a straight or branched alkylsulfonamido group which may preferably have 1 to 20 carbon atoms or a benzenesulfonamido group, a carbamoyl group, a straight or branched alkylaminocarbonyl group which may preferably have 1 to 20 carbon atoms or a phenylaminocarbonyl group, a sulfamoyl group, a straight or branched alkylaminosulfonyl group which may preferably have 1 to 20 carbon atoms or a phenylaminosulfonyl group, and the like.

Next, representative exemplary compounds of the cyan coupler represented by formula (C - I) or (C - II) will be shown below, but the present invention is not limited by these compounds.

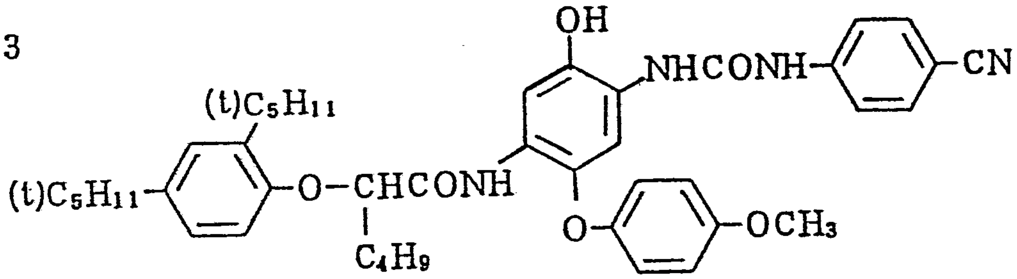
C - 1


OH
NHCONH
CN
(t)C5H11
(t)C5H11
O-CHCONH
C4H9

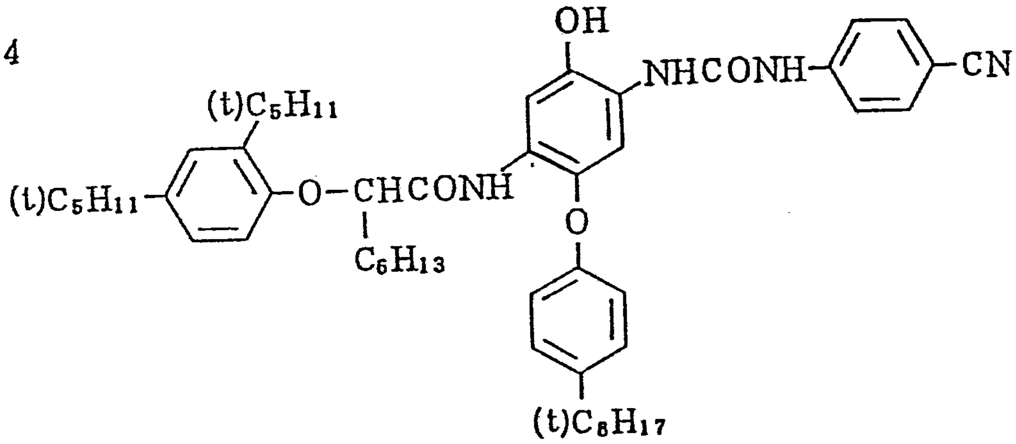
C - 2


OH
NHCONH
CN
(t)C5H11
O-CHCONH
C6H13(n)
(t)C5H11

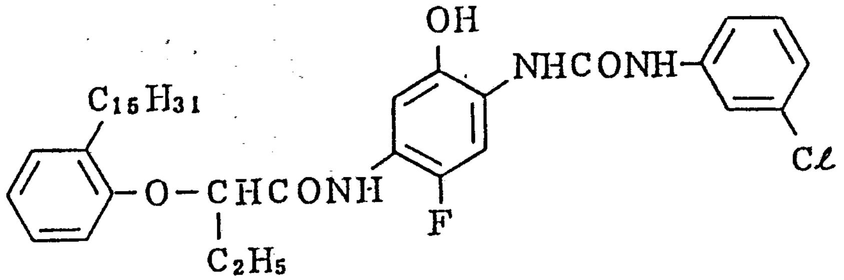
C - 3


OH
NHCONH
CN
(t)C5H11
(t)C5H11
O-CHCONH
C4H9
O
OCH3

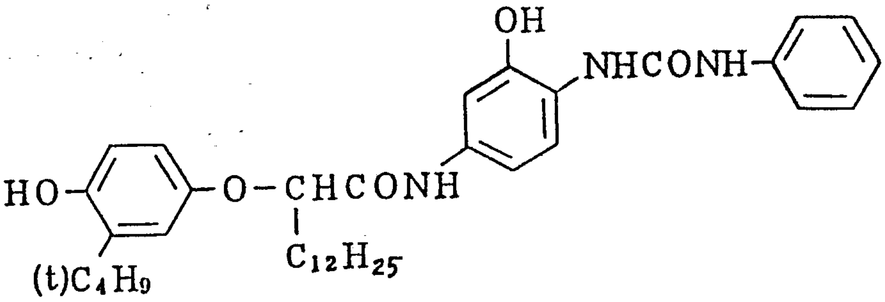
C - 4


OH
NHCONH
CN
(t)C5H11
(t)C5H11
O-CHCONH
C6H13
O
(t)C8H17

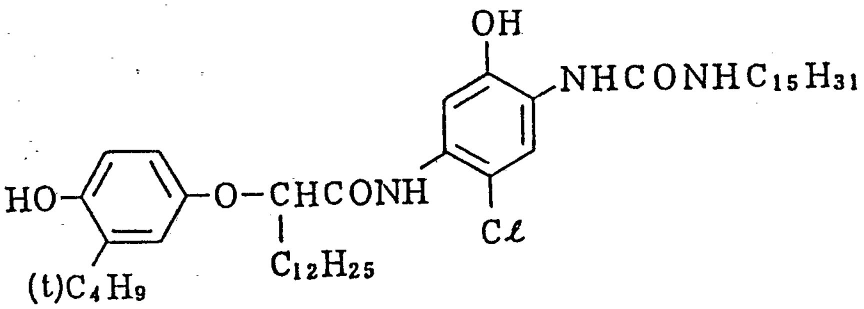
C - 5


OH
NHCONH
C₁₅H₃₁
Cℓ
O-CHCONH
F
C₂H₅

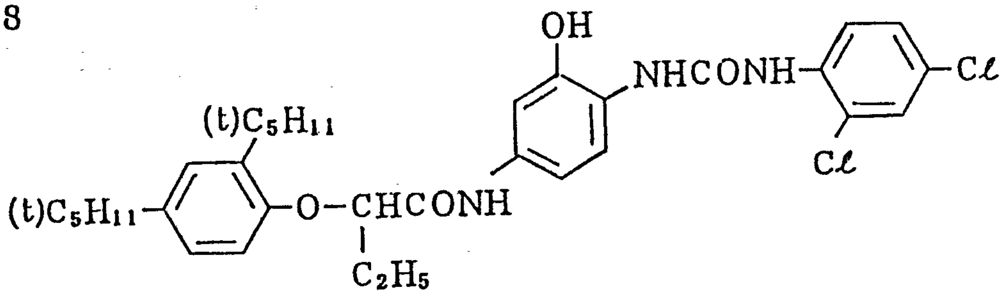
C - 6


OH
NHCONH
HO
O-CHCONH
C₁₂H₂₅
(t)C₄H₉

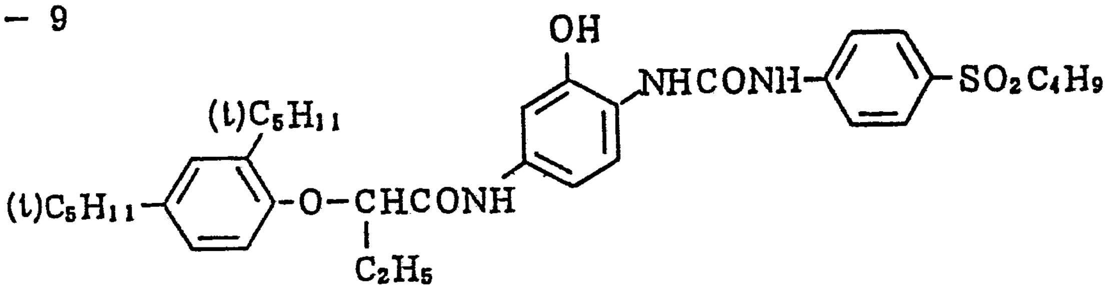
C - 7


OH
NHCONHC₁₅H₃₁
HO
O-CHCONH
Cℓ
C₁₂H₂₅
(t)C₄H₉

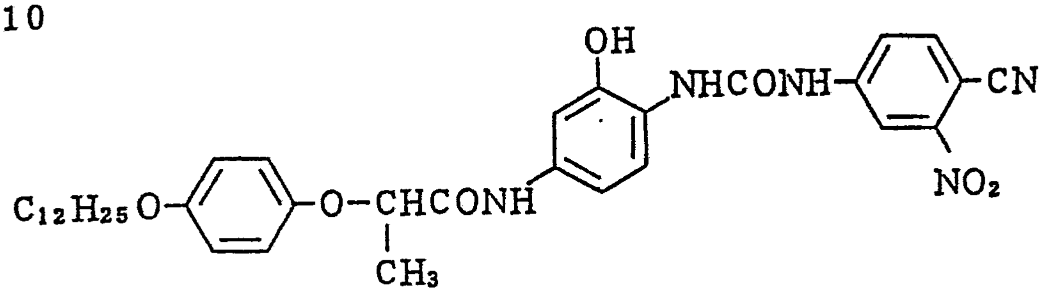
C - 8


OH
NHCONH
Cℓ
(t)C₅H₁₁
Cℓ
(t)C₅H₁₁
O-CHCONH
C₂H₅

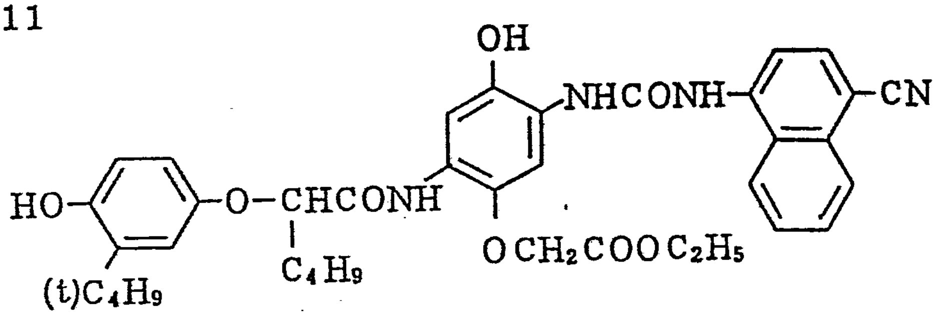
C - 9



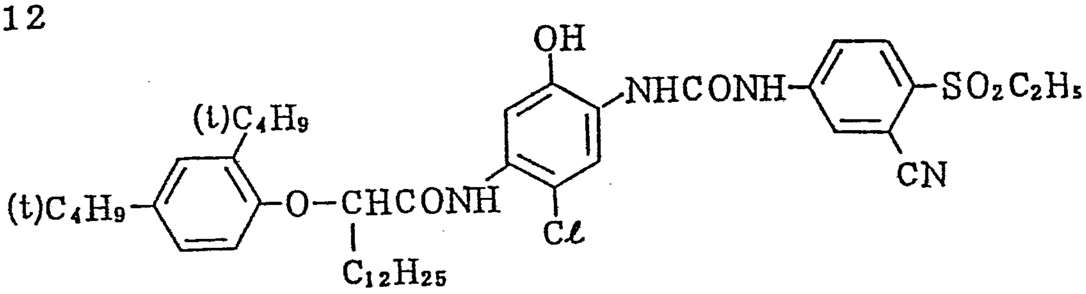
C - 10



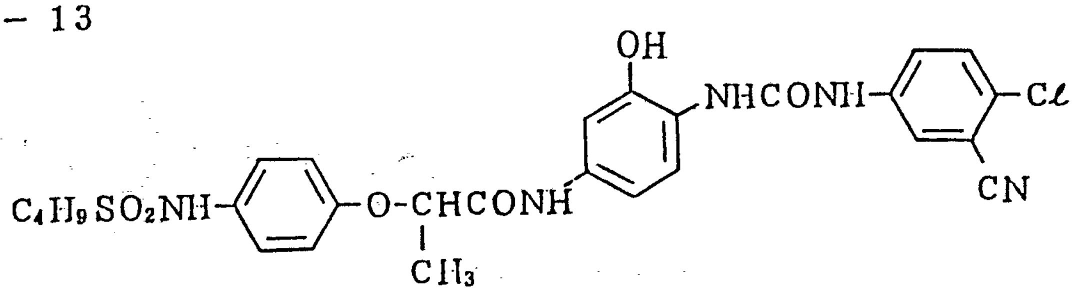
C - 11



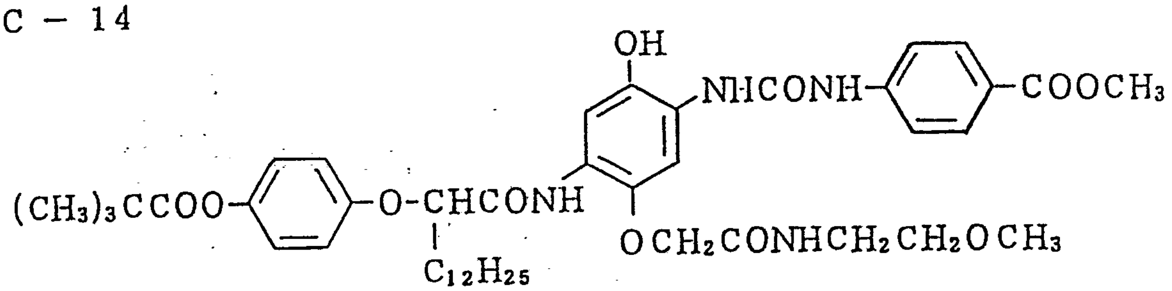
C - 12



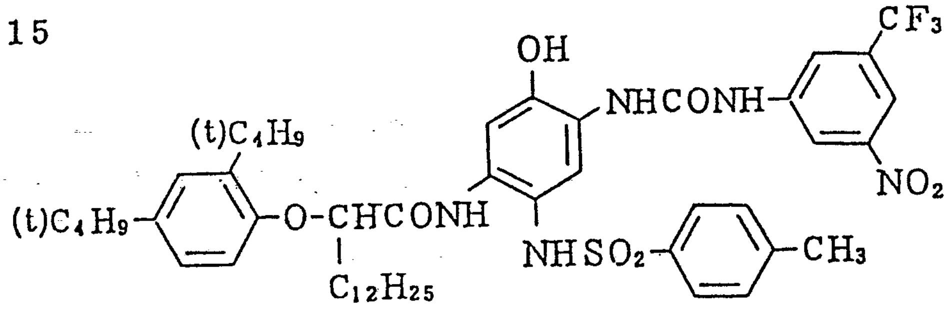
C − 13



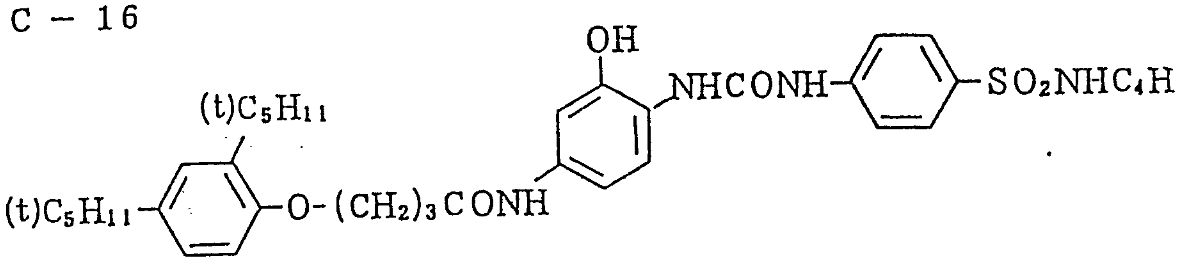
C − 14



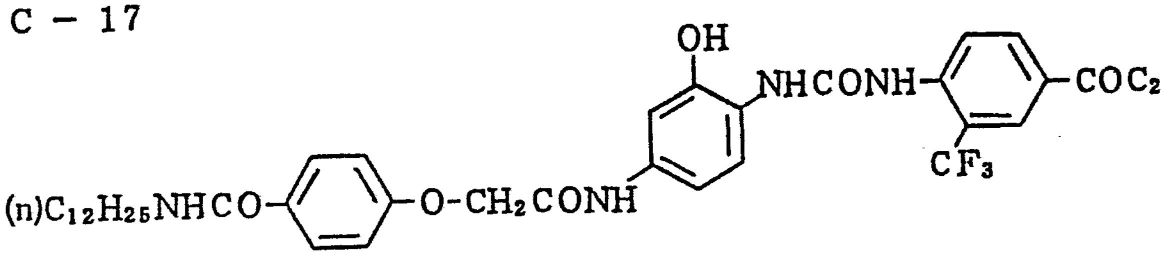
C − 15



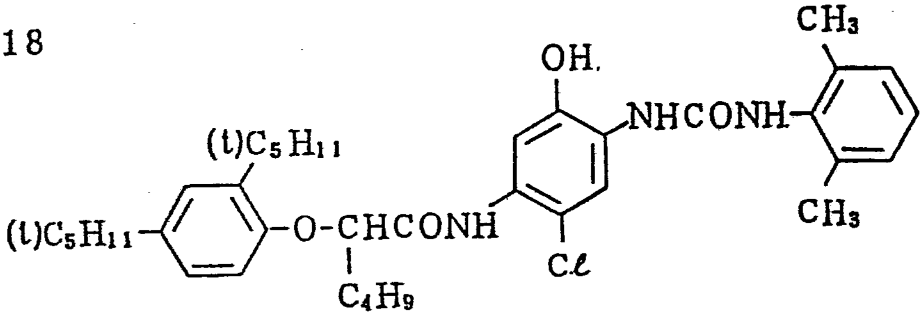
C − 16



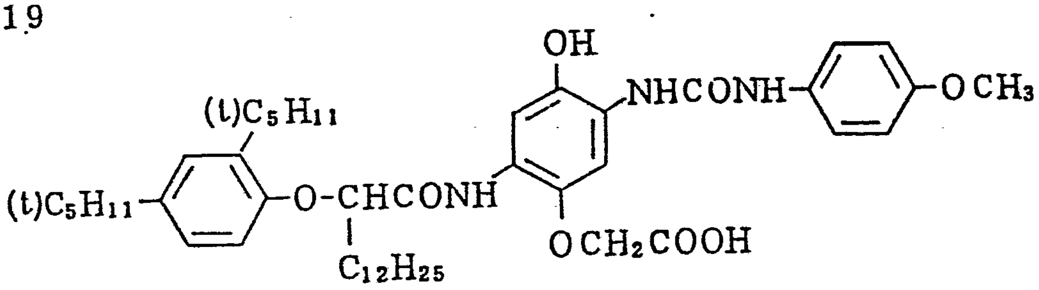
C - 17



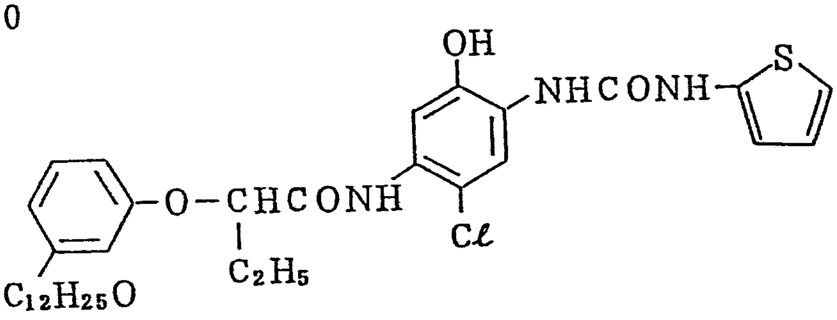
C - 18



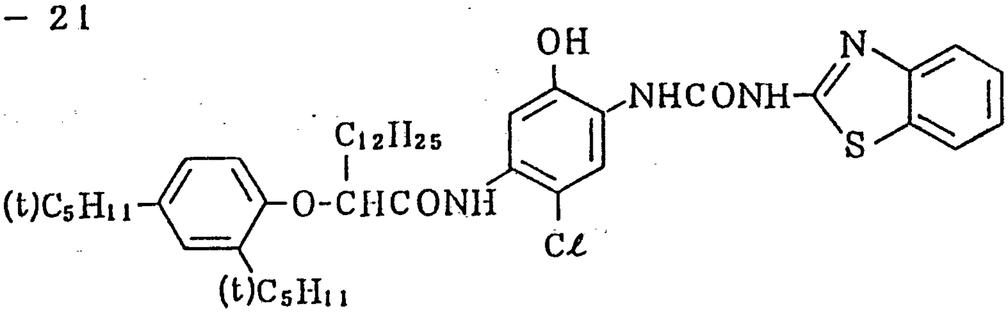
C - 19



C - 20



C − 21



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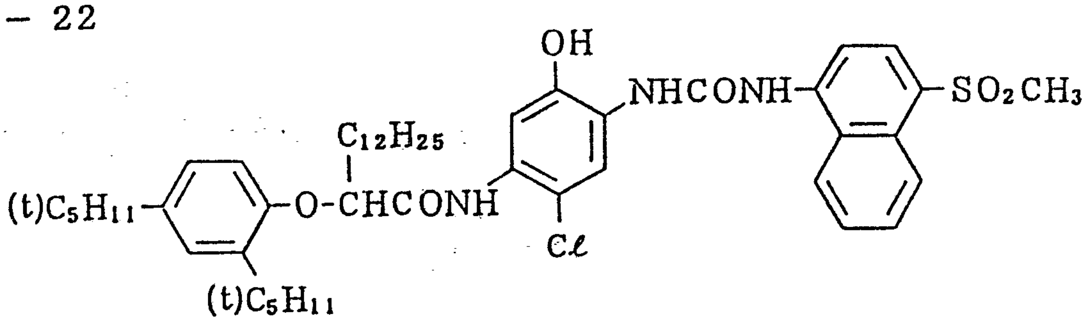

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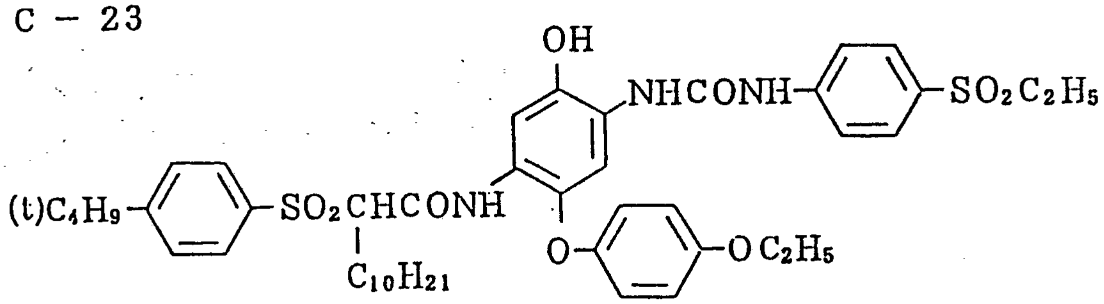

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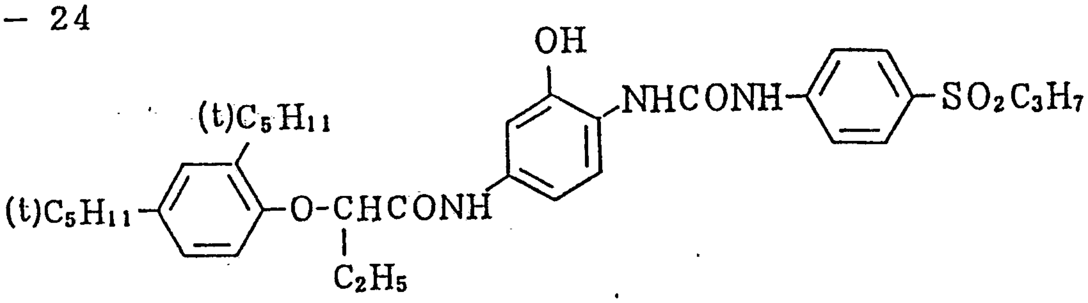

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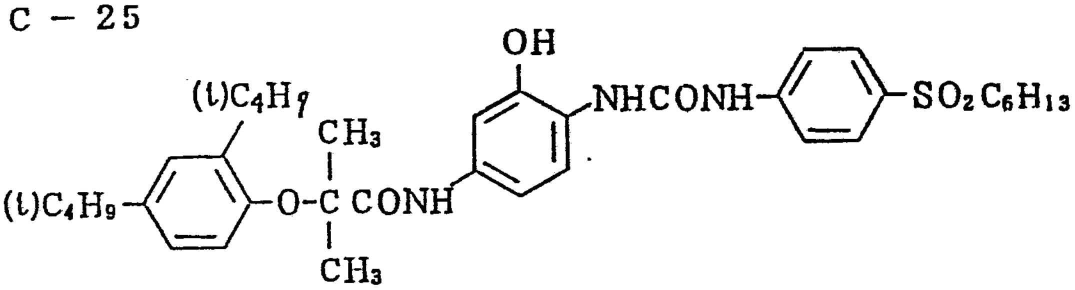

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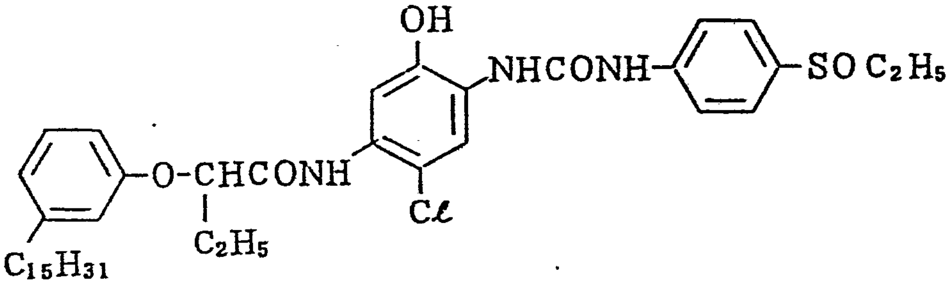

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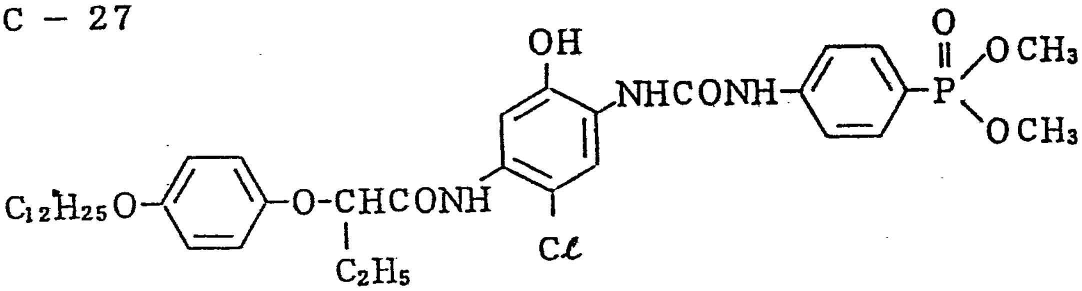
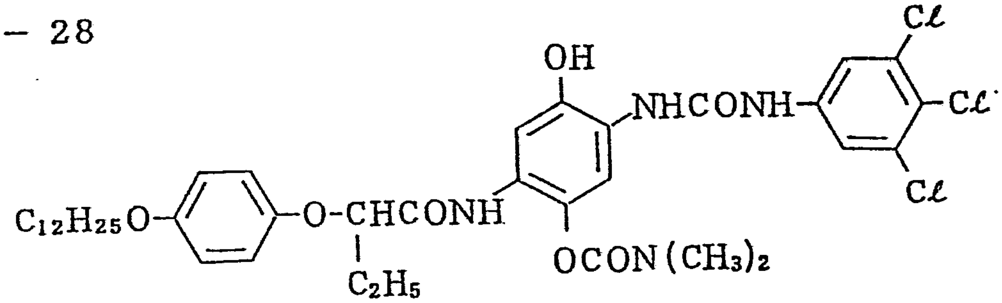
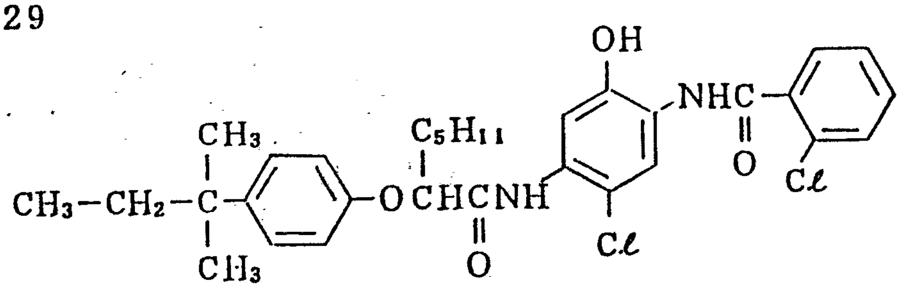


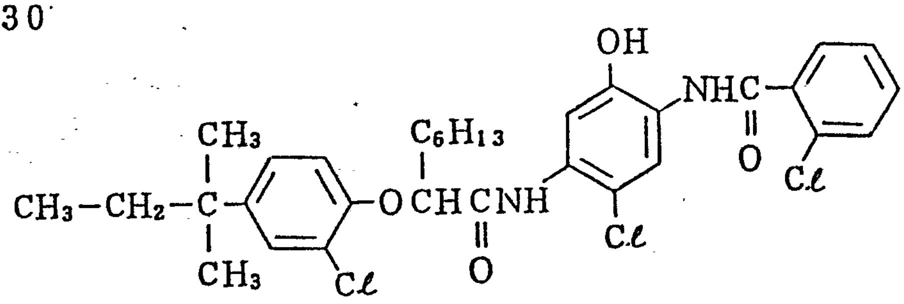
C - 28



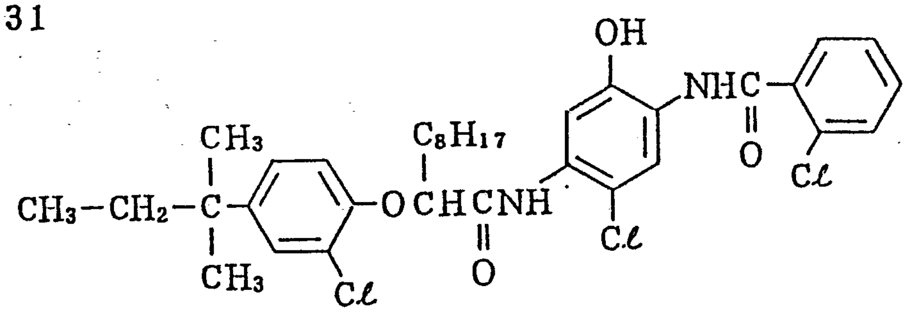
C - 29



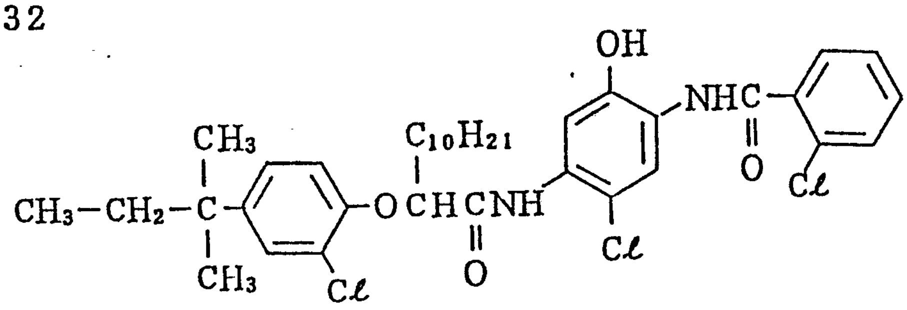
C - 30



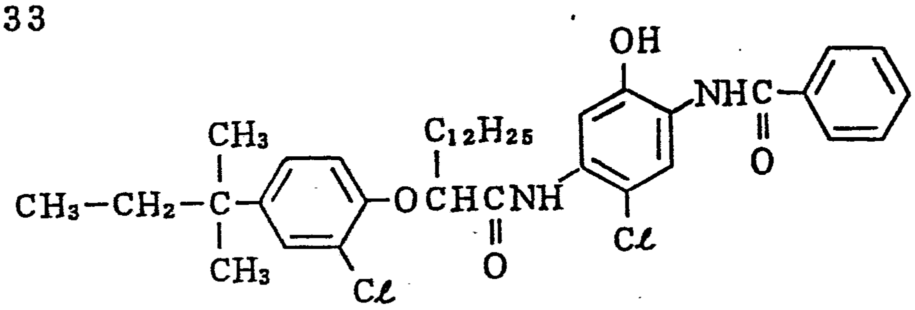
C - 31



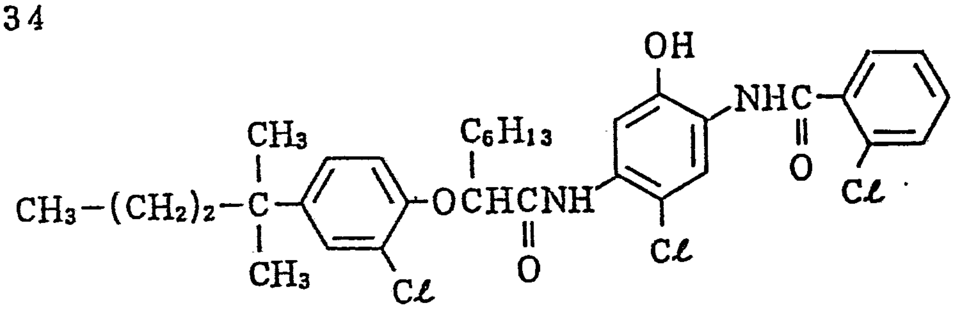
C - 32



C - 33



C - 34



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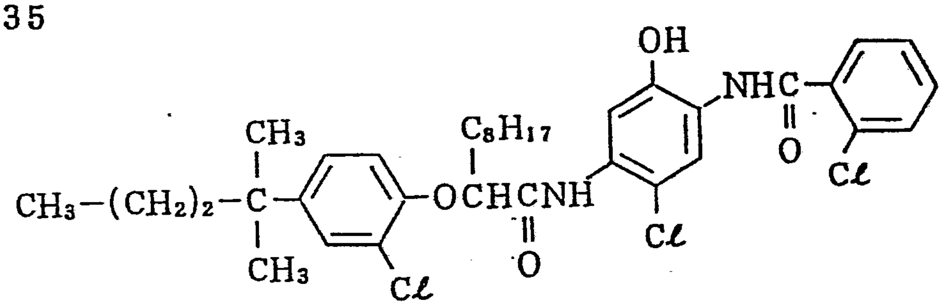
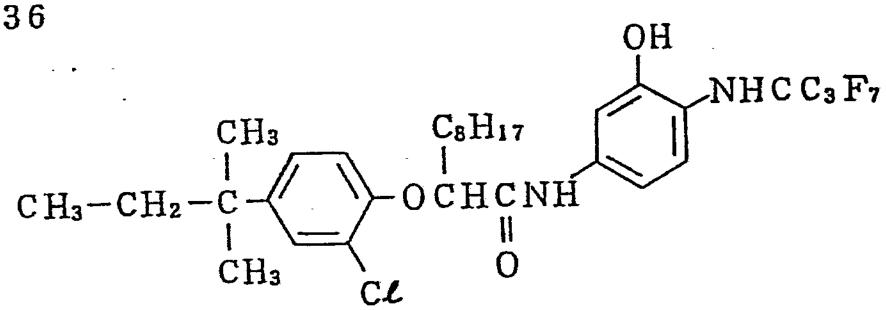
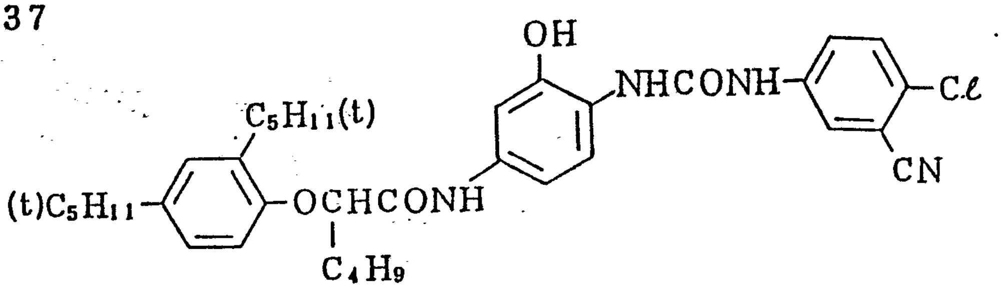


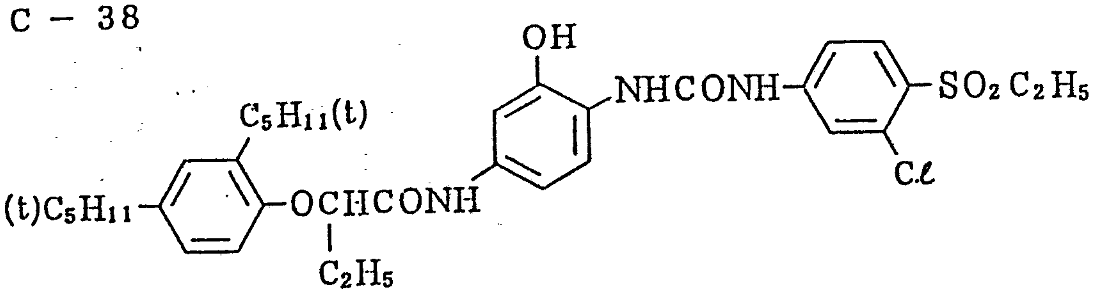
C - 36



C − 37



C − 38



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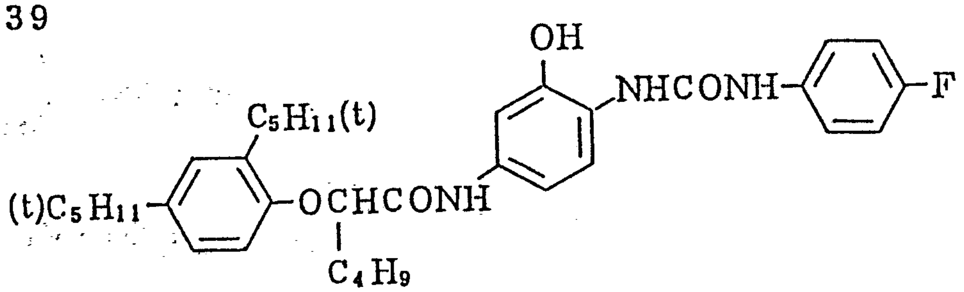

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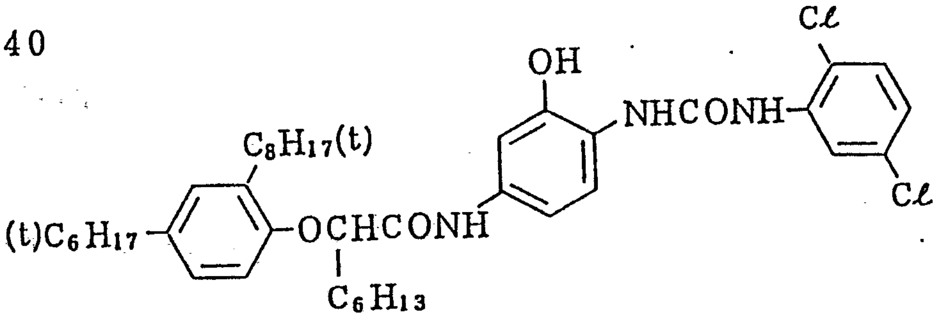

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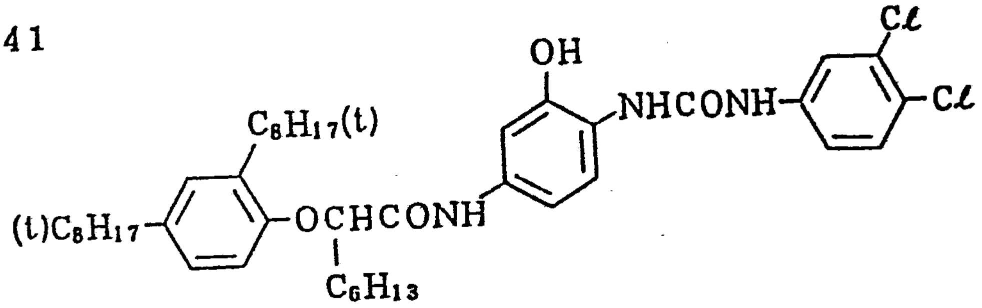

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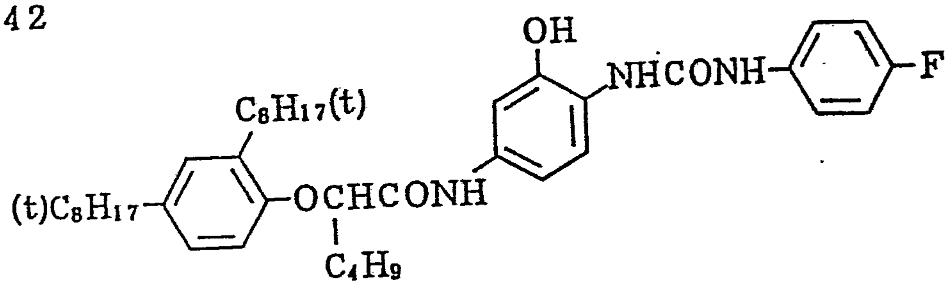

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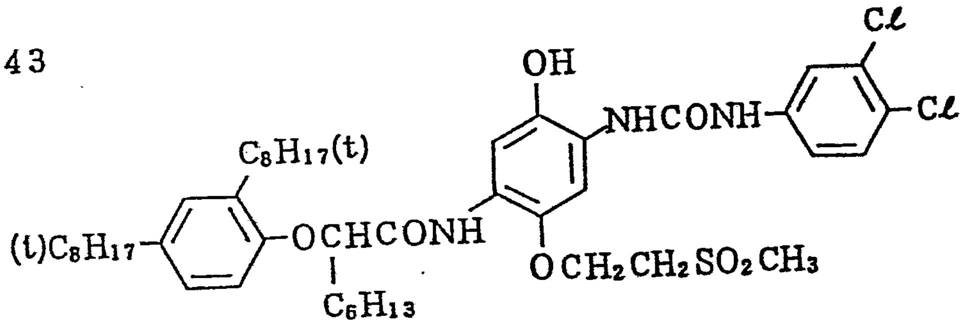

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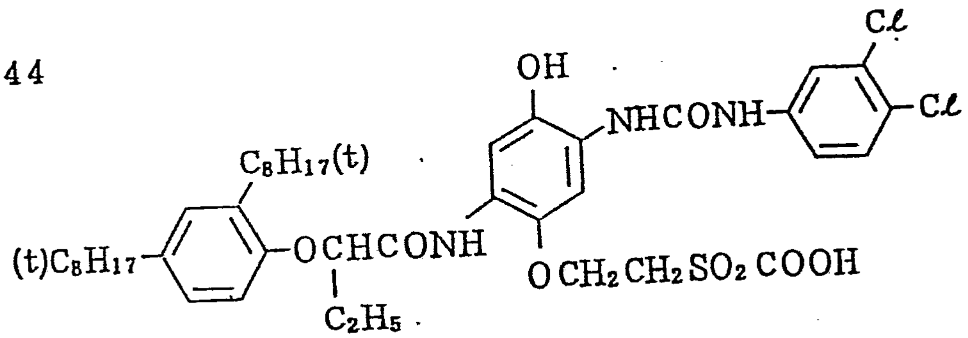

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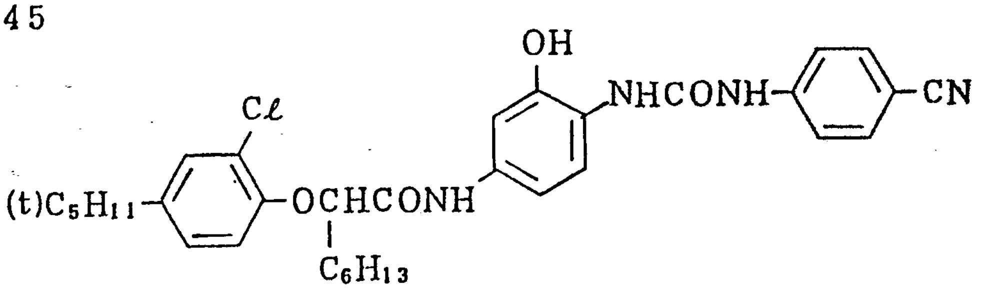

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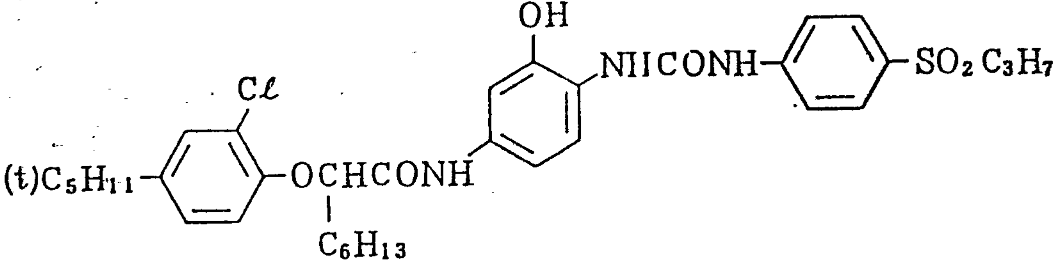

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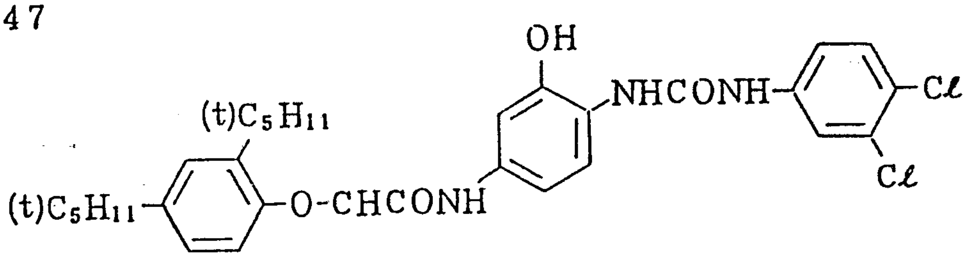

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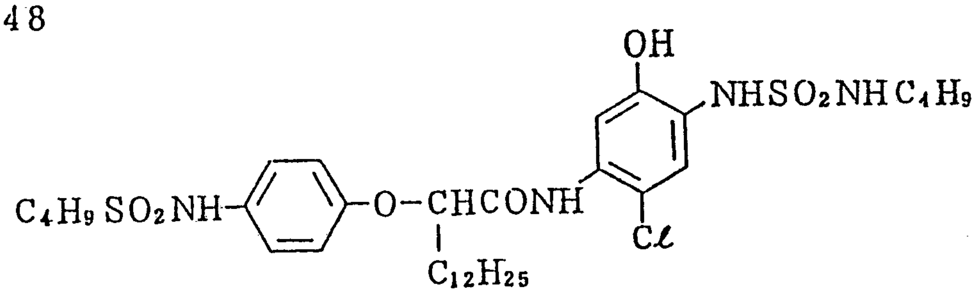

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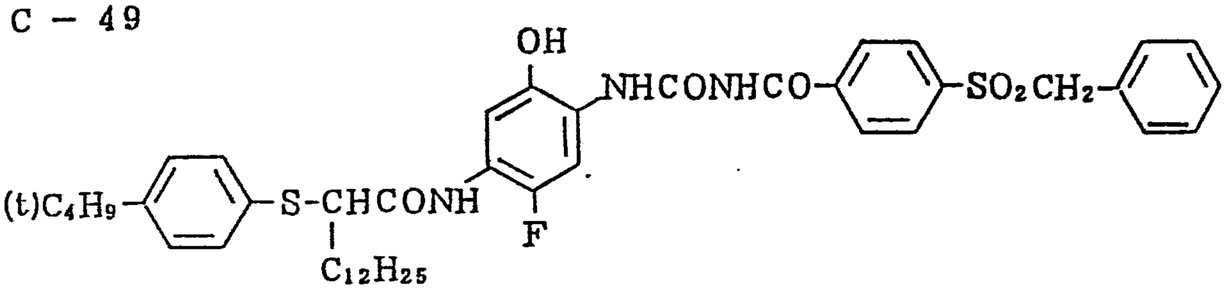

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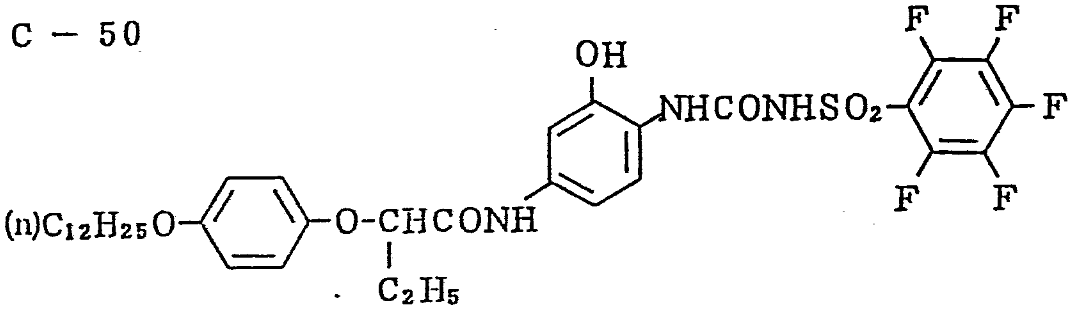

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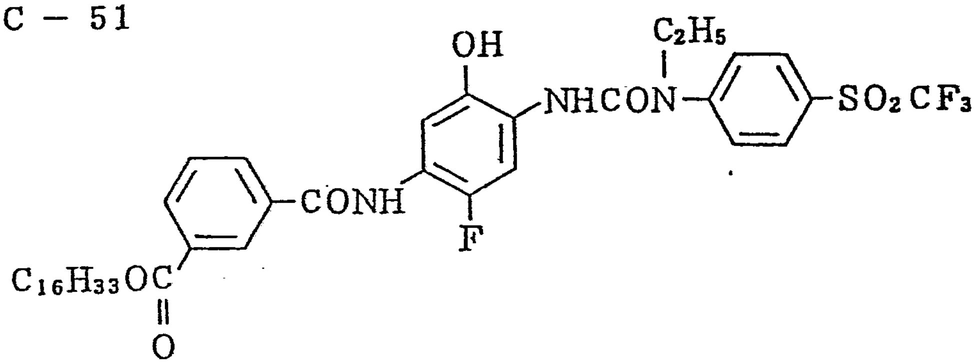

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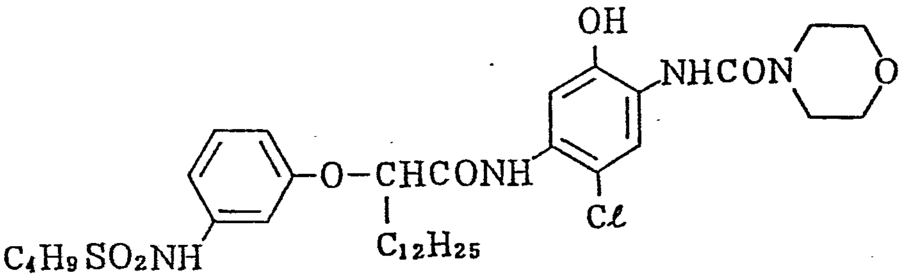

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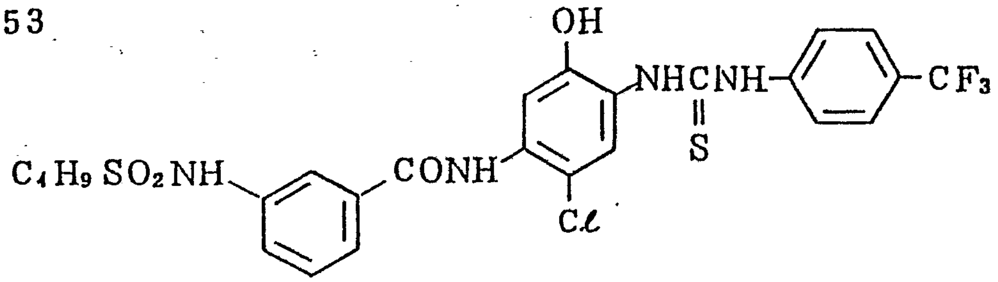

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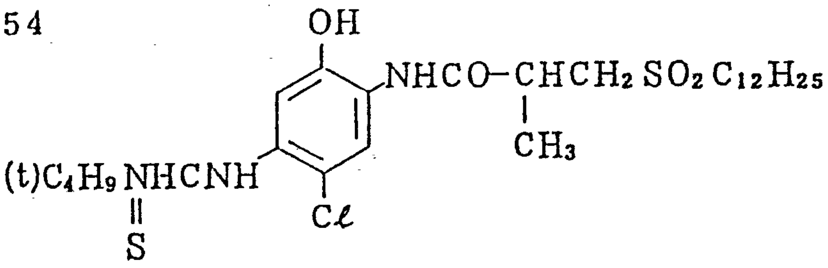

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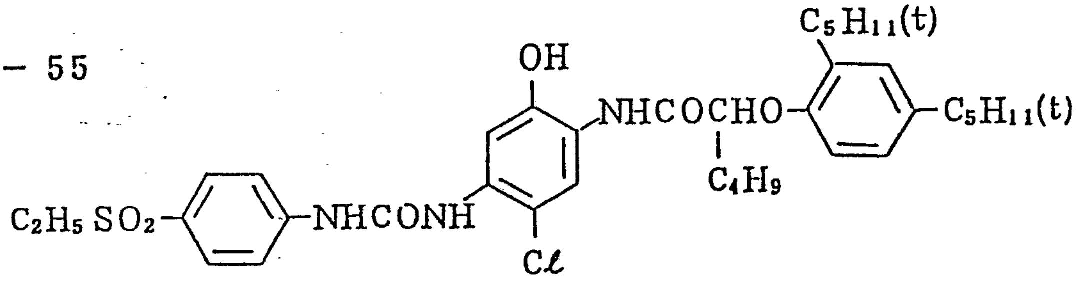

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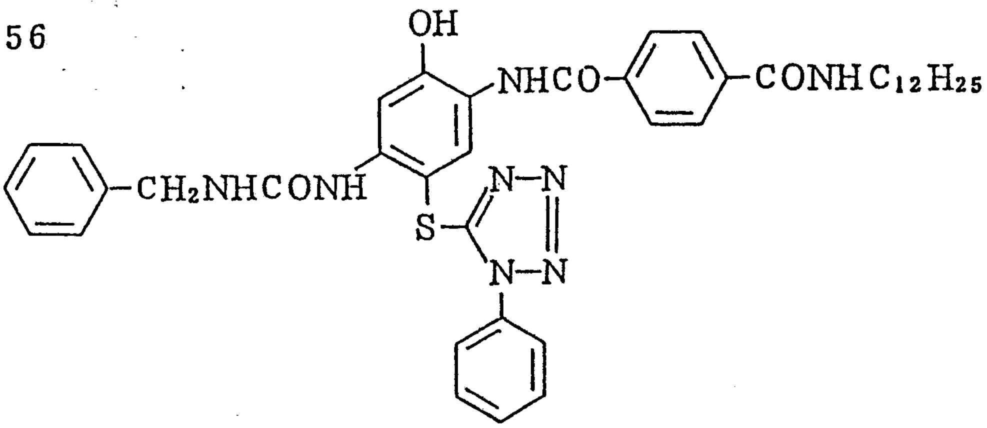

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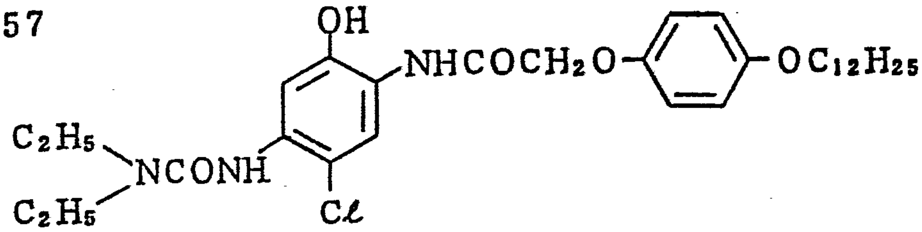

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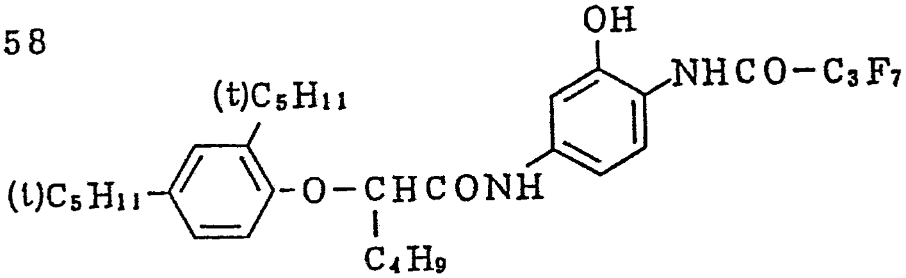

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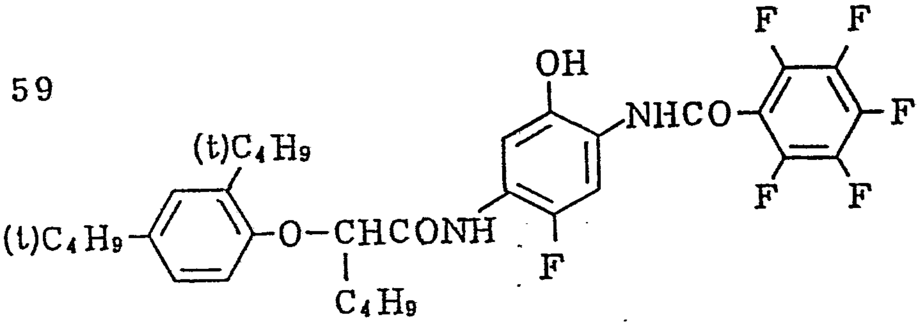

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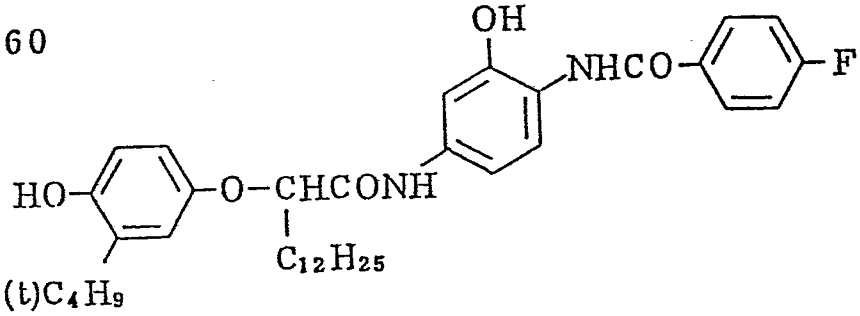

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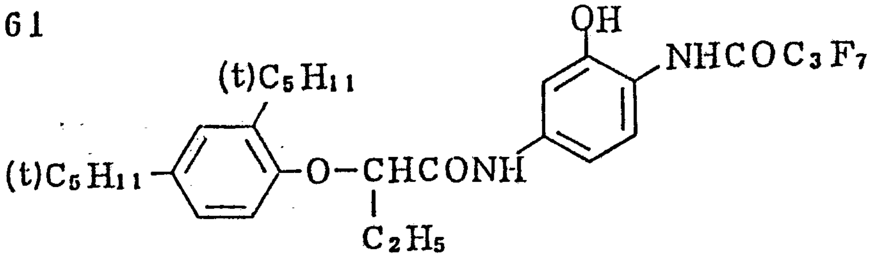

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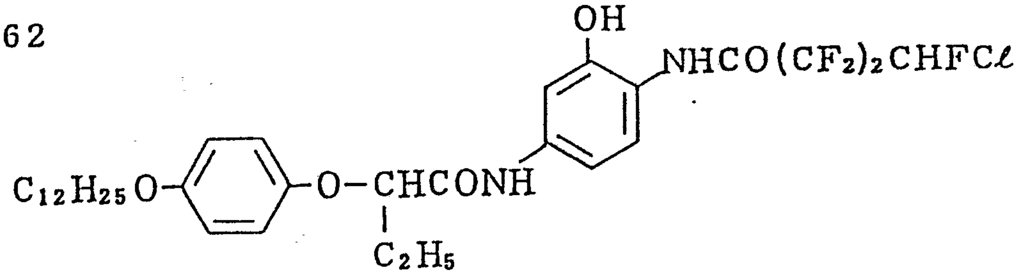

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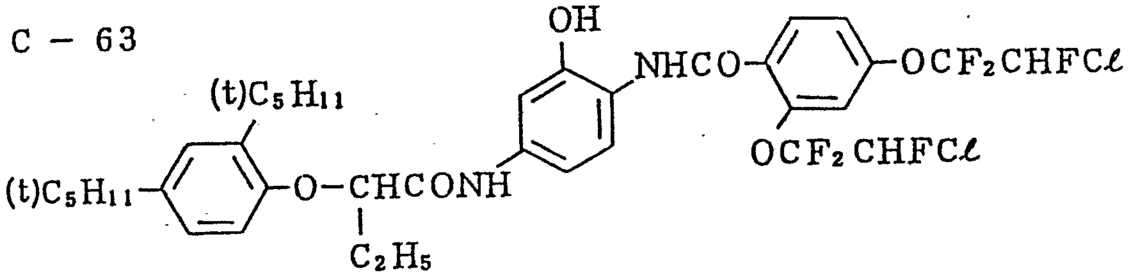

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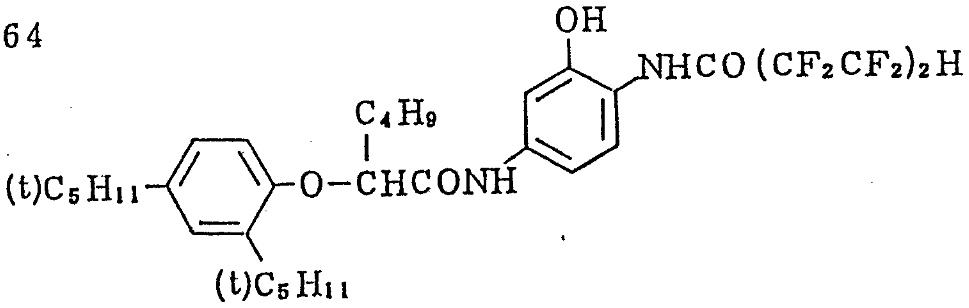

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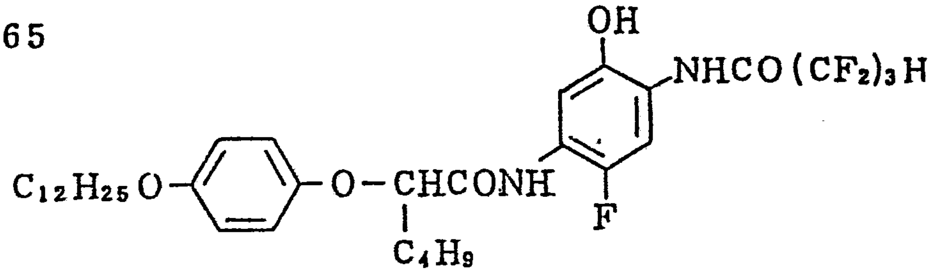

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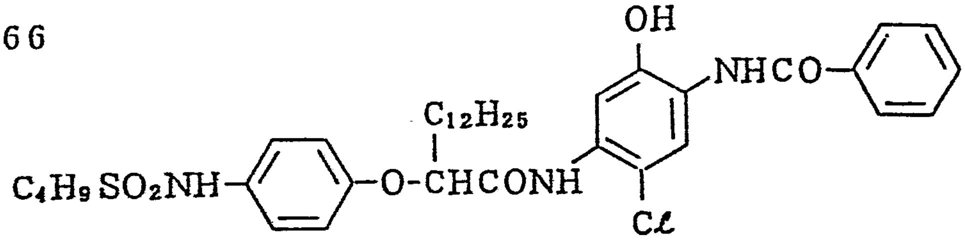

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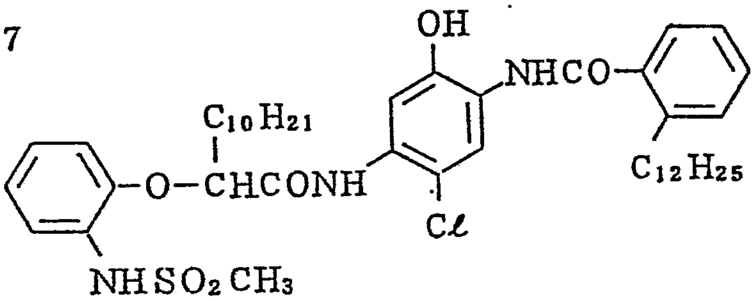

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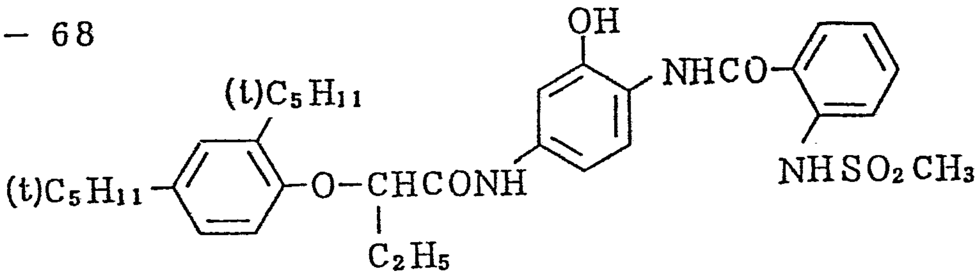

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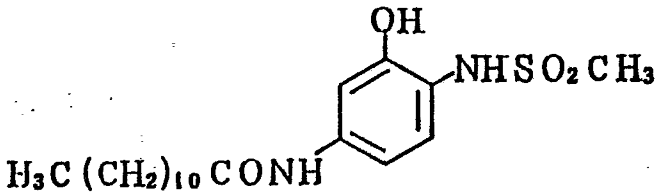

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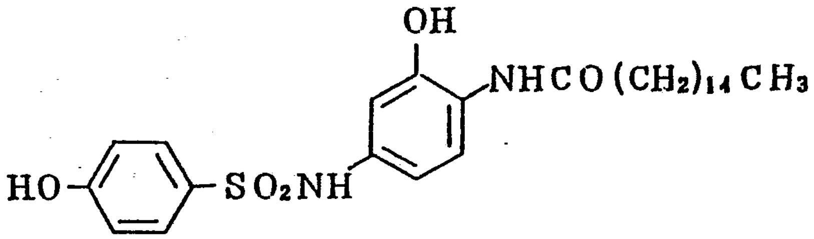

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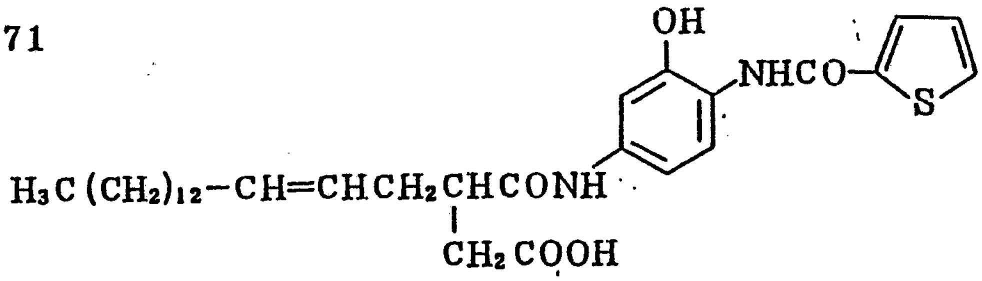

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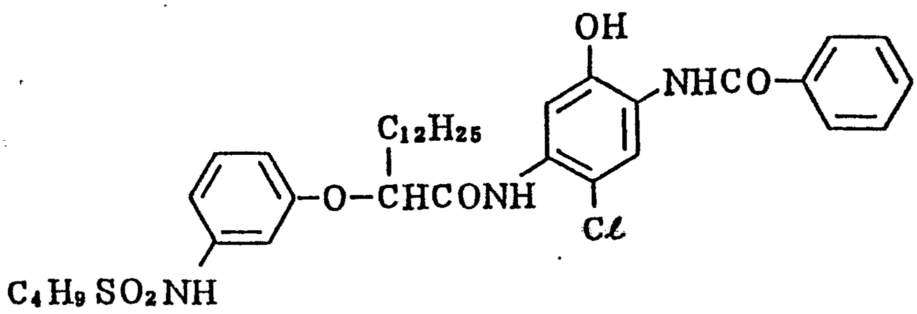

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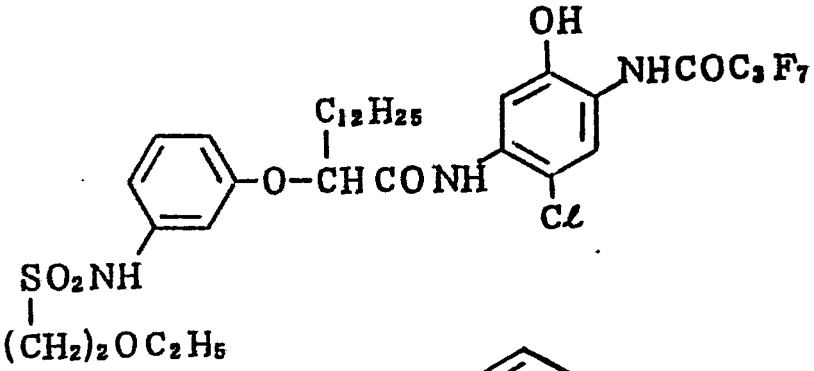

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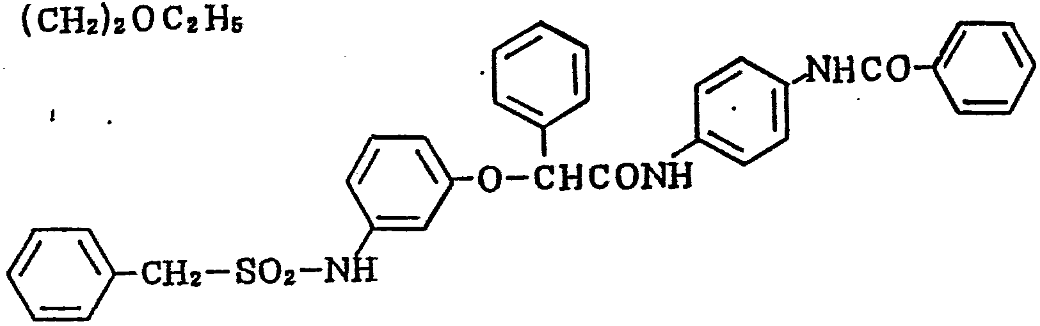

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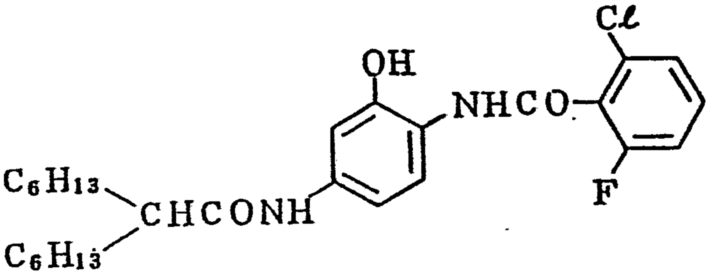

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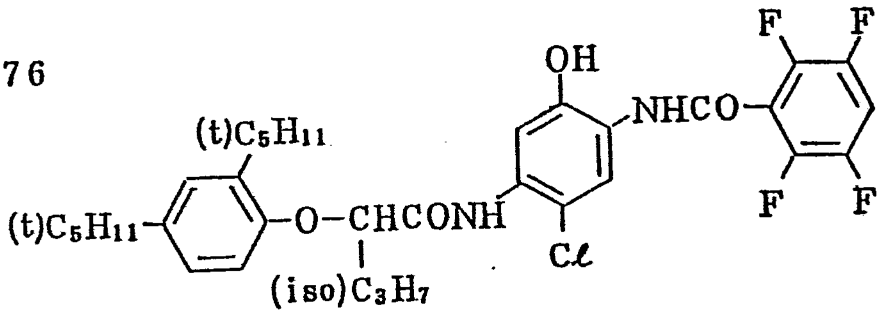

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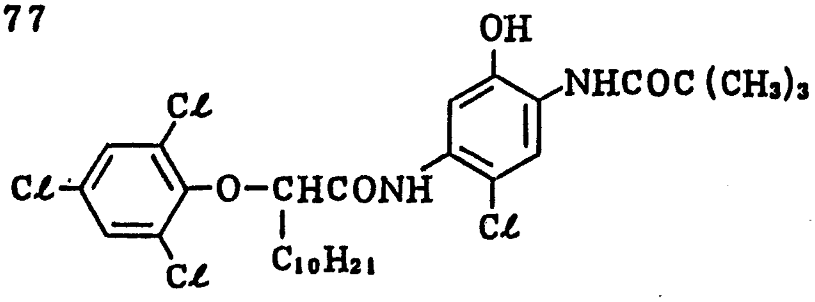

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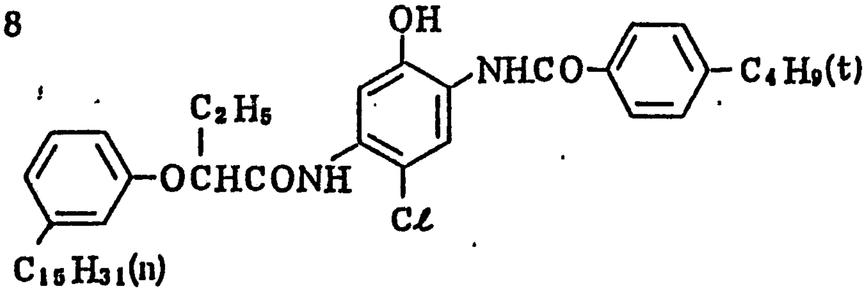

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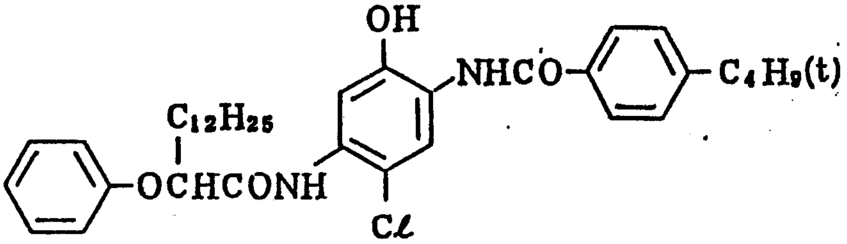

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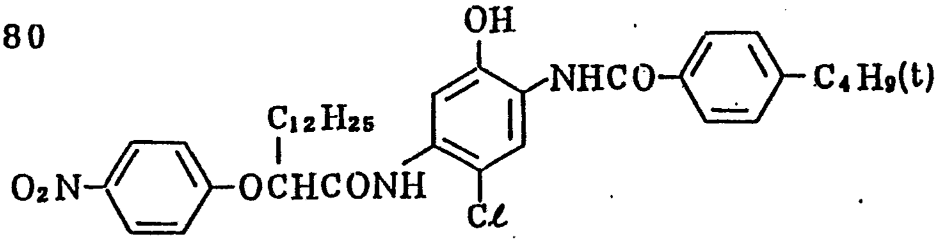

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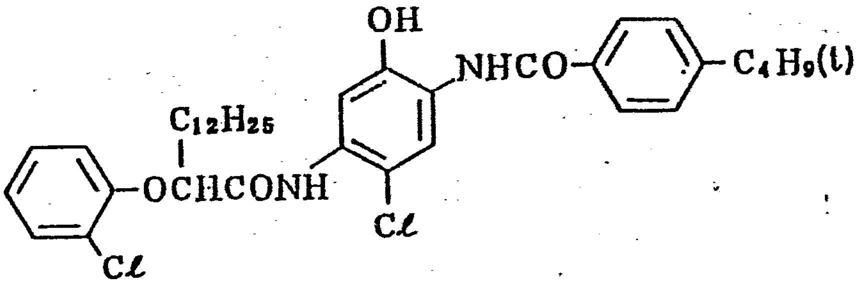

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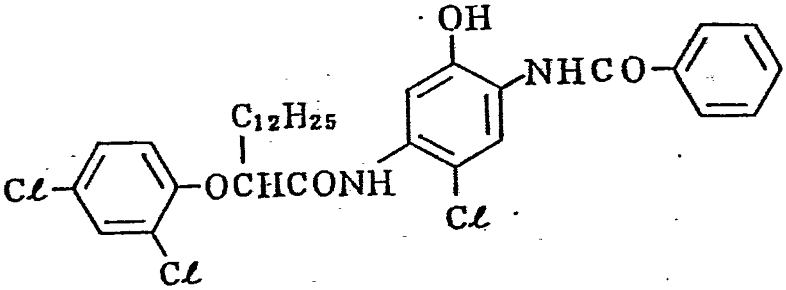

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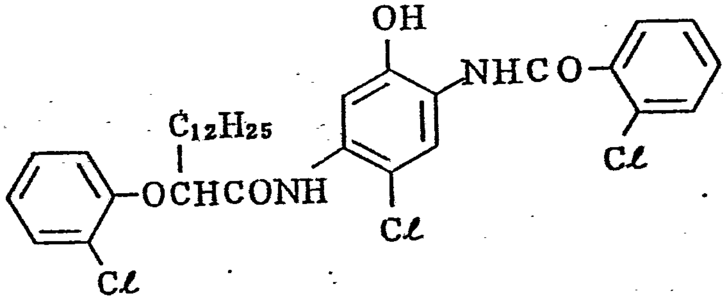

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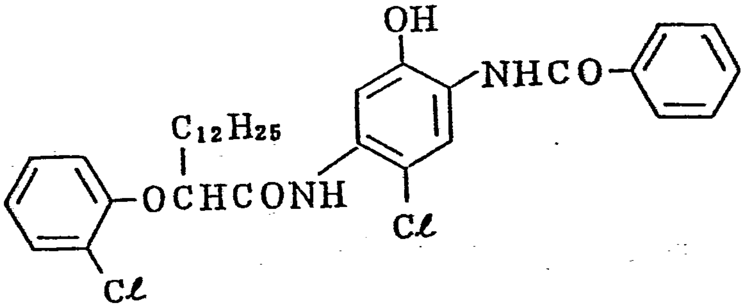

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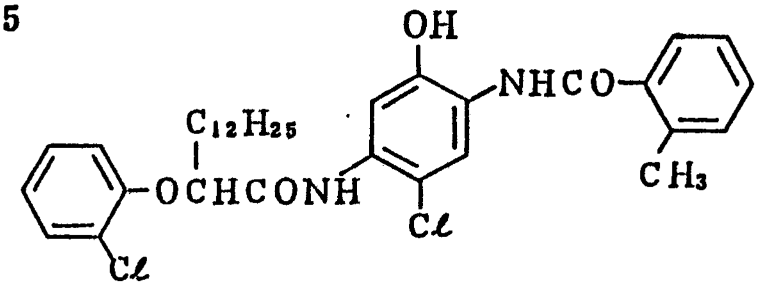

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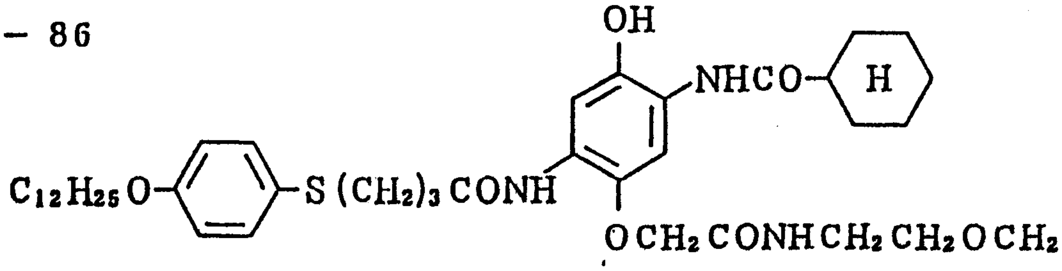

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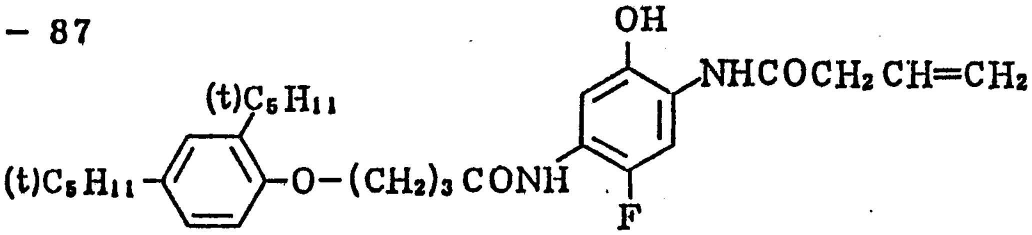

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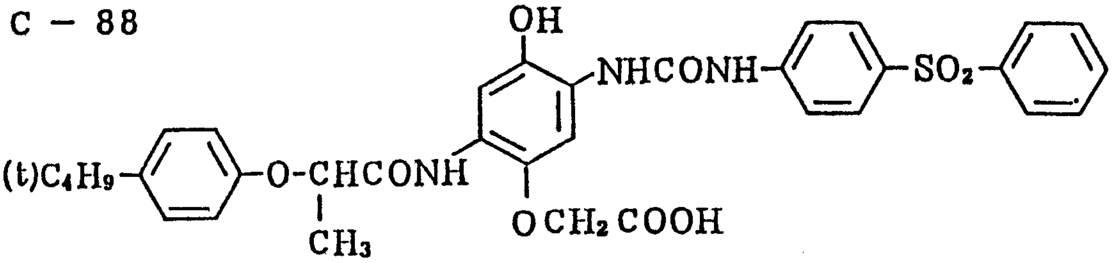

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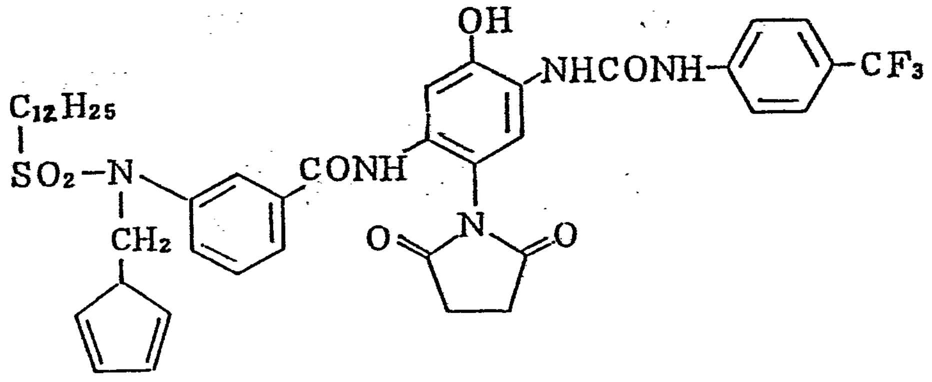

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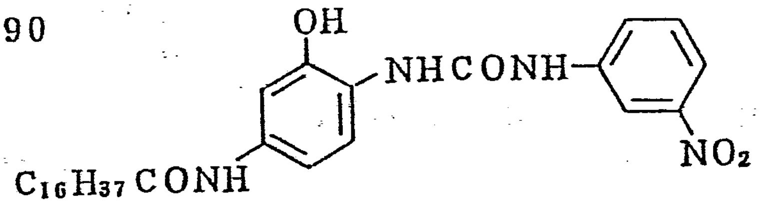

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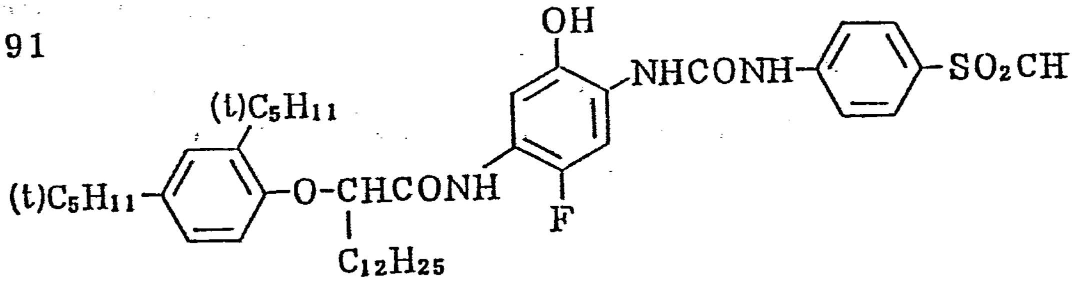

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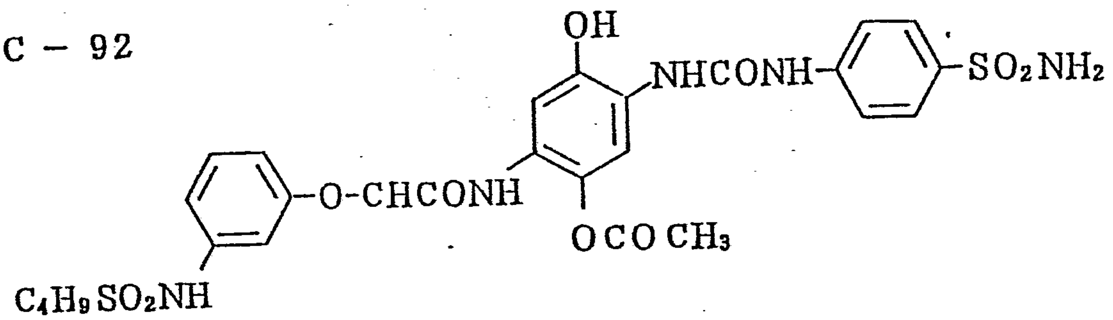

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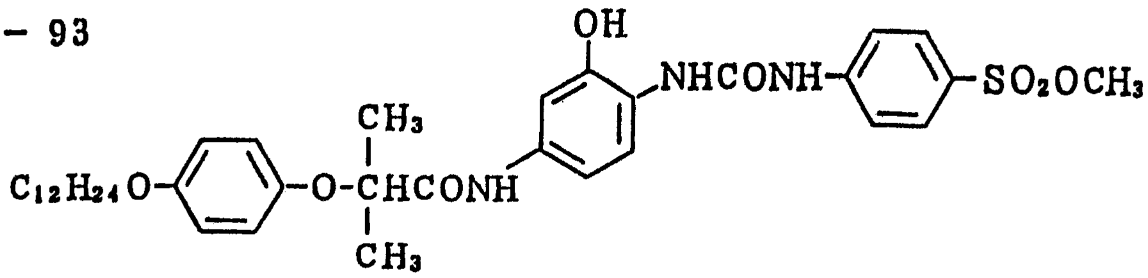

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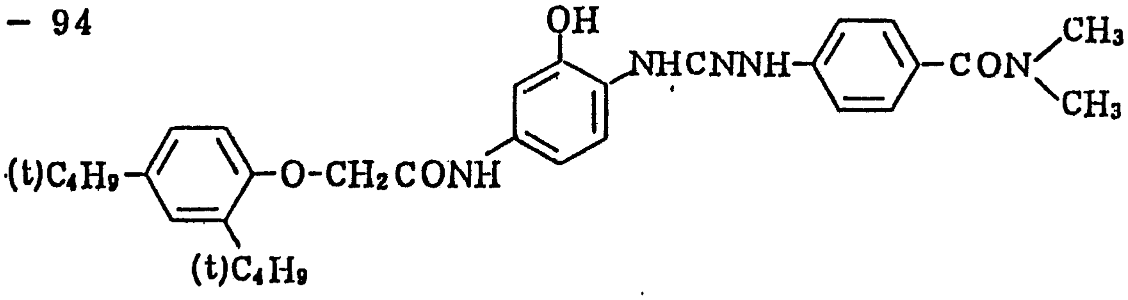

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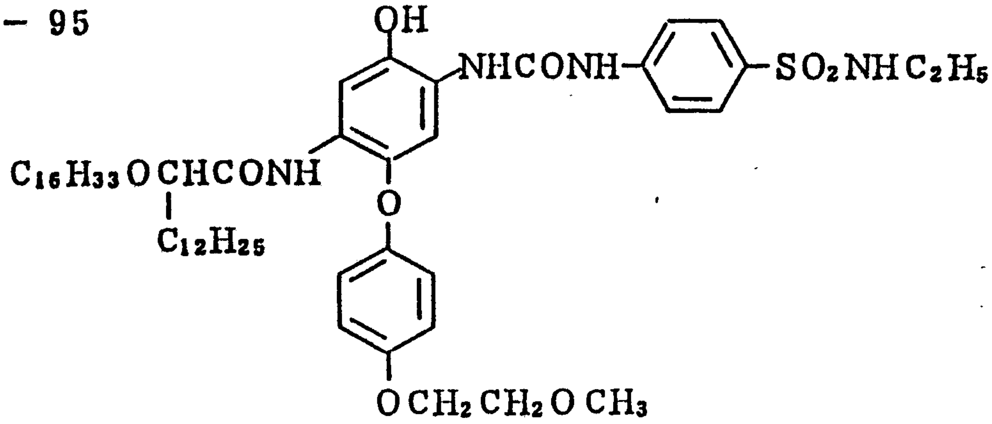

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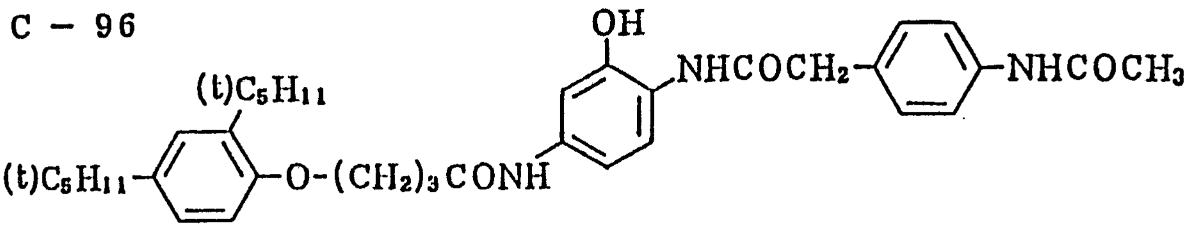

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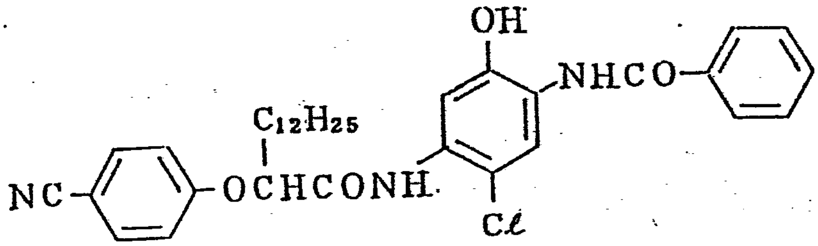

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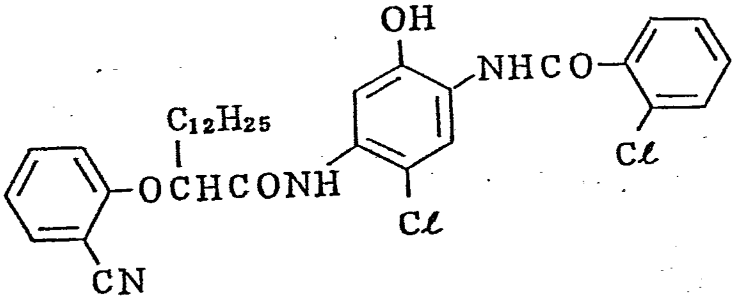

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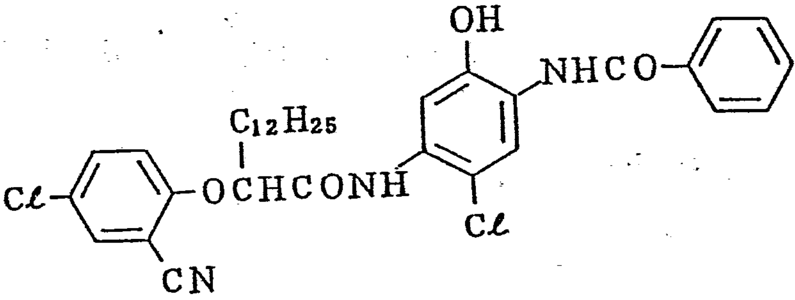

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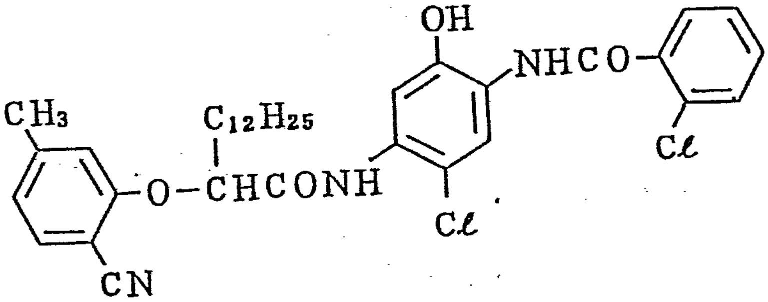
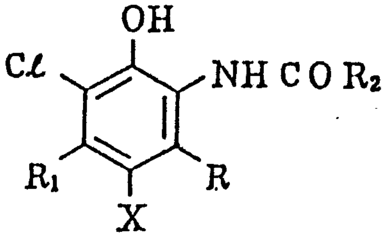


These cyan couplers of Formula (C-I) or (C-II) can be synthesized by the known method, and for example, they can be synthesized by the methods as disclosed in U.S. Patent Nos. 2,772,162, 3,758,308, 3,880,661, 4,124,396, 3,222,176, British Patent No. 975,773, 8,011,693 and 8,011,694; Japanese Unexamined Patent Publication Nos. Nos. 21139/1972, 112038/1975, 163537/1980, 29235/1981, 99341/1980, 116030/1981, 69329/1977, 55945/1981, 80045/1981 and 134644/1975; British Patent No. 1,011,940; U.S. Patent Nos. 3,446,622 and 3,996,253; Japanese Unexamined Patent Publication Nos. 65134/1981, 204543/1982, 204544/1982, 204545/1982, 33249/1983, 33251/1983, 33252/1983, 33250/1983, 33248/1983, 46645/1984, 31334/1983, 146050/1984, 166956/1984, 24547/1985, 35731/1985, 37557/1985 and so on.

The cyan couplers represented by Formulae (C-I) and (C - III) in accordance with the present invention is typically used in an amount of about 0.005 to 2 moles, preferably 0.01 to 1 mole per one mole of silver.

Next, the cyan coupler represented by Formula (C-III) will be described in detail.



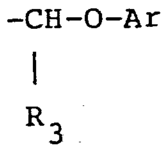
(C - III)

In formula (C - III), one of R and R_1 represents a hydrogen atom and the other is a straight or branched alkyl group having 2 to 12 carbon atoms; X represents a hydrogen atom or a group eliminatable through the coupling reaction with an oxidized product of N-hydroxyalkyl substituted-p-phenylenediamine derivative color developing agent; and R_2 represents a ballast group.

In the present invention, the straight or branched alkyl group having 2 to 12 carbon atoms represented by R_1 and R of the above formula (C - III) are, for example, an ethyl group, a propyl group, a butyl group.

In the formula (C - III), the ballast group represented by R_2 is an organic group having a size and form which affords a coupler molecule bulkiness sufficient to substantially prevent the coupler from diffusing from the layer in which it has been contained to the other layers. As the representative ballast group, there may be mentioned an alkyl group or an aryl group each having total carbon atoms of 8 to 32, preferably those having total carbon atoms of 13 to 28. As the substituent for the alkyl group and the aryl group, there may be mentioned, for example, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a carboxy group, an acyl group, an ester group, a hydroxy group, a cyano group, a nitro group, a carbamoyl group, a carbonamide group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfonamide group, a sulfamoyl group, a halogen atom and the like, and as the substituent for the alkyl group, those as mentioned for the above aryl group except for the alkyl group.

Preferred ballast groups are represented by the following formula:



$$-\underset{R_3}{\underset{|}{\mathrm{CH}}}-\mathrm{O}-\mathrm{Ar}$$

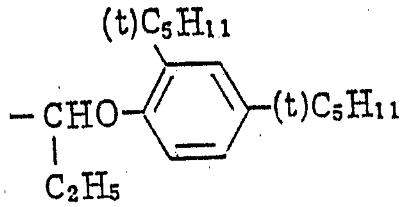
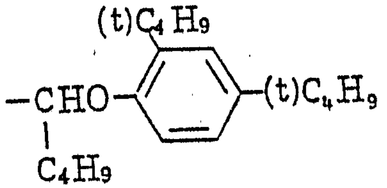
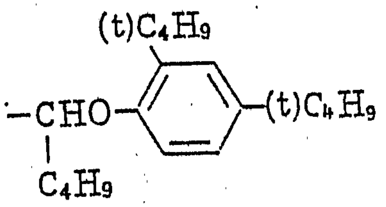
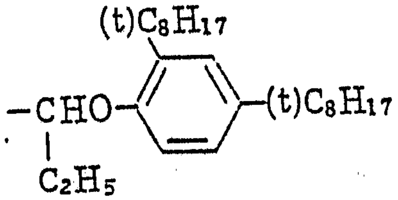
R_3 represents an alkyl group having 1 to 12 carbon atoms; and Ar represents an aryl group such as a phenyl group, etc. and the aryl group may have a substituent. As the substituent, an alkyl group, a hydroxy group, a halogen atom, an alkylsulfonamido group, etc. may be mentioned and the most preferred is a branched alkyl group such as a t-butyl group, etc.

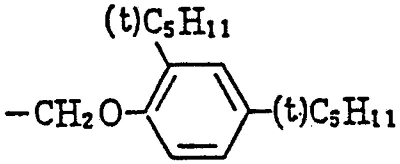
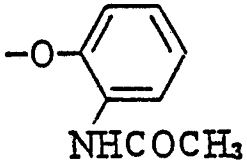
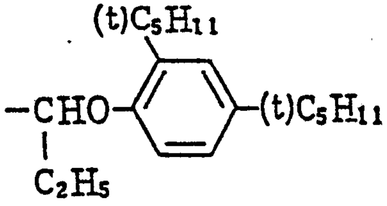
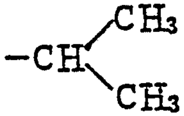
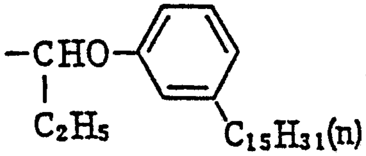
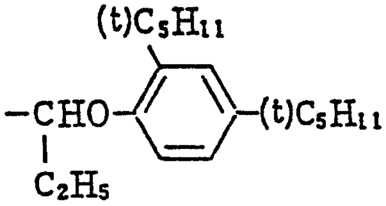
The group represented by x in the above formula (C - III), which is capable of being released through the coupling reaction, determines not only the equivalence number of the coupler but also the reactivity thereof, as well known to one skilled in the art.

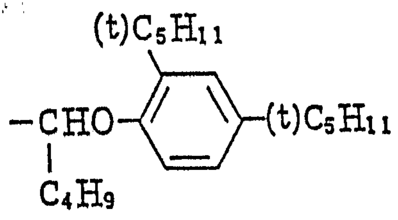
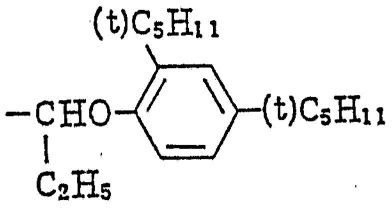
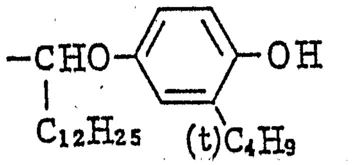
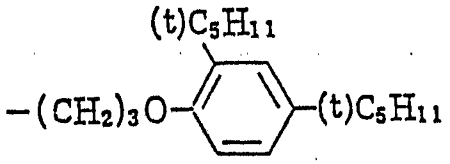
The representative examples for x includes halogen represented by chlorine and fluorine, an aryloxy group, a substituted or unsubstituted alkoxy group, an acyloxy group, a sulfonamido group, an arylthio group, a heteroylthio group, a heteroyloxy group, a sulfonyloxy group, a carbamoyloxy group and the like. As specific examples for x, there may be mentioned the groups as disclosed in Japanese Unexamined Patent Publication Nos. 10135/1975, 120334/1975, 130441/1975, 48237/1979, 146828/1976, 14736/1979, 37425/1972, 123341/1975 and 95346/1983, Japanese Patent Publication No. 36894/1973; and U.S. Patent Nos. 3,476,563, 3,737,316 and 3,227,551.

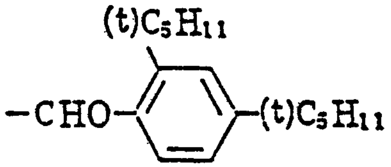
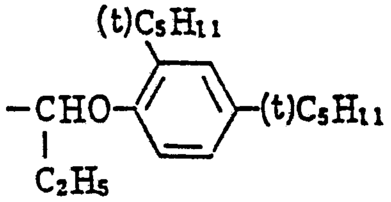
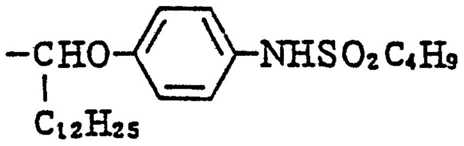
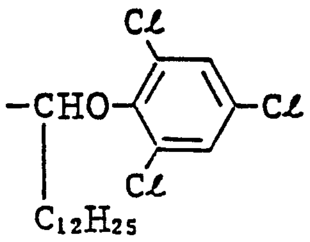
Next, exemplary compounds of the cyan coupler represented by formula (C - III) are shown below in such a manner that Rl, X, R2 and R are specified respectively, but the present invention is not limited by these compounds.

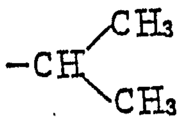
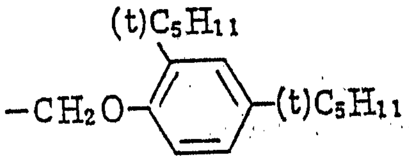
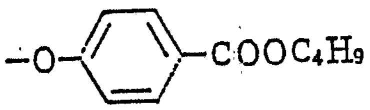
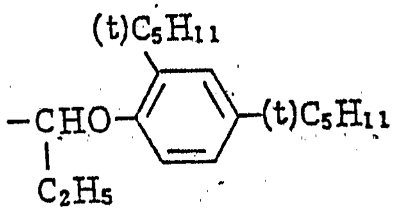
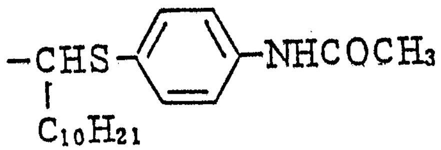
Exemplary Compounds

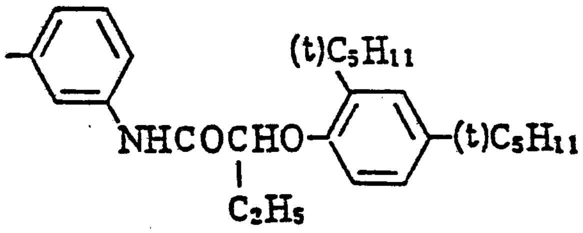
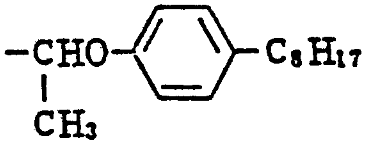
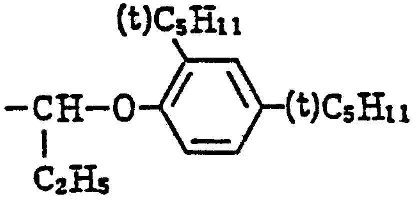
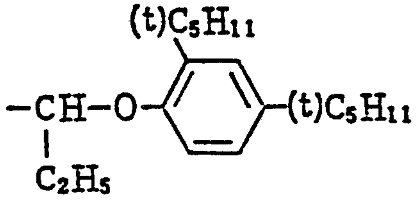
Coupler No.	R_1	X	R_2	R
C - 101	$-C_2H_5$	$-H$		$-H$
C - 102	$-C_2H_5$	$-C\ell$		$-H$
C - 103	$-C_2H_5$	$-H$		$-H$
C - 104	$-C_2H_5$	$-C\ell$		$-H$

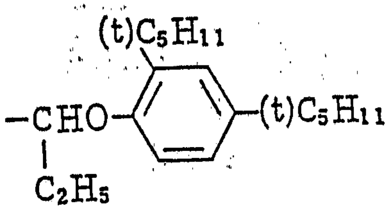
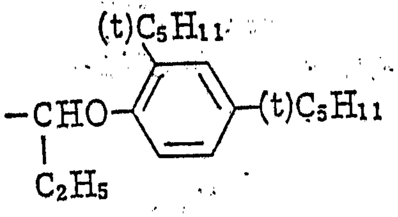
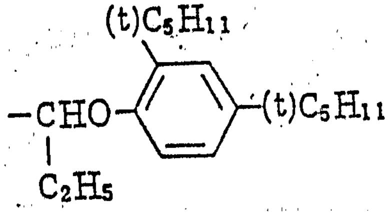
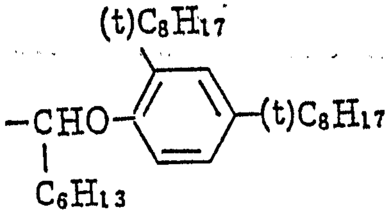
Coupler No.	R_1	X	R_2	R
C－105	$-C_2H_5$	$-Cl$		$-H$
C－106	$-C_2H_5$			$-H$
C－107	 $-CH(CH_3)_2$	$-Cl$		$-H$
C－108	$-C_2H_5$	$-Cl$		$-H$

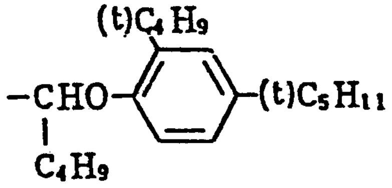
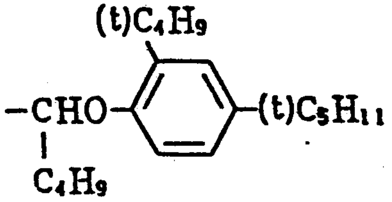
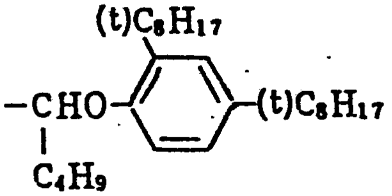
Coupler No.	R_1	X	R_2	R
C-109	$-C_2H_5$	$-C\ell$		$-H$
C-110	$-C_4H_9$	$-F$		$-H$
C-111	$-C_2H_5$	$-F$		$-H$
C-112	$-C_2H_5$	$-C\ell$		$-H$

Coupler No.	R_1	X	R_2	R
C-113	$-C_2H_5$	−F		−H
C-114	$-C_4H_9$	−Cℓ		−H
C-115	$-C_2H_5$	−Cℓ		−H
C-116	$-C_2H_5$	−Cℓ		−H

Coupler No.	R_1	X	R_2	R
C－117		$-Cl$	$-C_{18}H_{37}$	$-H$
C－118	$-C_2H_5$	$-F$		$-H$
C－119	$-C_2H_5$			$-H$
C－120	$-C_2H_5$	$-Cl$		$-H$

Coupler No.	R_1	X	R_2	R
C-121	$-C_3H_7$	$-Cl$		$-H$
C-122	$-C_3H_7$	$-Cl$		$-H$
C-123	$-C_2H_4NHCOCH_3$	$-Cl$		$-H$
C-124	$-C_3H_6OCH_3$	$-Cl$		$-H$

Coupler No.	R_1	X	R_2	R
C－125	$-H$	$-Cl$		$-C_2H_5$
C－126	$-H$	$-Cl$		$-C_3H_7$
C－127	$-H$	$-Cl$		$-C_5H_{11}$
C－128	$-C_2H_5$	$-Cl$		$-H$

Coupler No.	R_1	X	R_2	R
C − 129	$-C_2H_5$	−Cℓ		−H
C − 130	$-C_2H_5$	−H		−H
C − 131	$-C_2H_5$	−Cℓ		−H

In the following, the synthesis method for obtaining some of the exemplary compounds of Formula (C -III) are shown, but the other exemplary compounds can also be synthesized similarly.

Synthesis of Exemplary compound C - 101

[(1) - a] Synthesis of 2-nitro-4,6-dichloro-5-ethylphenol

In 150 ml of glacial acetic acid were dissolved 33 g of 2-nitro-5-ethylphenol, 0.6 g of iodine and 1.5 g of ferric chloride. To the mixture was added dropwise 75 ml of sulfuryl chloride at 40 °C over 3 hours. After completion of the dropwise addition of the sulfuryl chloride, precipitates formed during the dropwise addition are reacted and dissolved by heating under reflux.

It took about 2 hours for the heating under reflux. Then, the reaction mixture was poured into water and the formed crystals were purified by recrystallization from methanol. Confirmation of (1) - a was carried out by the nuclear magnetic resonance spectrum and the elemental analysis.

[(1) - b] Synthesis of 2-amino-4,6-dichloro-5-ethylphenol

In 300 ml of alcohol was dissolved 21.2 g of the above compound [(1) - a], and to the solution was added a catalytic amount of Raney nickel and hydrogen was passed therethrough under ambient pressure until no hydrogen absorption was observed. After the completion of the reaction, the Raney nickel was removed and the alcohol was distilled out under reduced pressure. The resulting residue was employed in the next acylation step without purification.

[(1) - c] Synthesis of 2-[(2,4-di-tert-acylphenoxy)-acetamido]-4,6-dichloro-5-ethylphenol

In a mixed solution comprising 500 ml of glacial acetic acid and 16.7 g of sodium acetate was dissolved a crude amino derivative obtained in [(1) - b], and to the resulting solution was added dropwise at room temperature an acetic acid solution which had dissolved 28.0 g of 2,4-di-tert-aminophenoxyacetic acid chloride in 50 ml of acetic acid. The acetic solution was added dropwise for 30 minutes, and after further stirring for 30 minutes, the reaction mixture was poured into ice-cold water. After the formed precipitates were collected by filtration and dried, recrystallized twice from acetnitrile to obtain the title compound. Identification of the title compound was carried out by the elemental analysis and the nuclear magnetic resonance spectrum.

$C_{21}H_{35}NO_3Cl_2$

	C	H	N	Cl
Calculated (%)	65.00	7.34	2.92	14.76
Observed (%)	64.91	7.36	2.99	14.50

The cyan coupler of formula (C - III) of this invention may be preferably added in an amount of 2 x 10^{-3} to 5 x 10^{-1} mole, more preferably 1 x 10^{-2} to 3 x 10^{-1} mole per 1 mole of silver contained in the red-sensitive silver halide emulsion layer, but the amount of cyan coupler of formula (C - III) is not limitative.

In the present invention, the above couplers (C - I) to (C - III) of this invention may be used with other cyan couplers in combination. As cyan couplers which may be used in combination, there may be included phenol type compounds, naphtol type compounds, etc. and may be selected from those described in US Patent Nos. 2,369,929, 2,434,272, 2,474,293, 2,895,826, 3,253,924, 3,034,892, 3,311,476, 3,386,301, 3,418,390, 3,458,315, 3,591,383, etc.

Synthesis methods of these compounds are also described in these publications.

In the present invention, the cyan couplers represented by the formulae (C - I) to (C - III) may be used in combination with the conventionally known cyan couplers so long as it does not contradict to the object of the present invention. Further, the cyan couplers represented by formulae (C - I) to (C - III) may be used in combination therewith.

Magenta couplers for photography may include compounds of pyrazolone type, pyrazolotriazole type, pyrazolinobenzimidazole type, and indazolone type. The pyrazolone type magenta couplers may include the compounds disclosed in U.S. Patents No. 2,600,788, No. 3,062,653, No. 3,127,269, No. 3,311,476, No. 3,419,391, No. 3,519,429, No. 3,558,318, No. 3,684,514 and No. 3,888,680, Japanese Unexamined Patent Publications No. 29639/1974, No. 111631/1974, No. 129538/1974 and No. 13041/1975, Japanese Patent Publications No. 47167/1978, No. 10491/1979 and No. 30615/1980. The pyrazolotriazole type magenta couplers may include the couplers disclosed in U.S. Patent No. 1,247,493 and Belgian Patent No. 792,525. As nondiffusion colored magenta couplers, there may be generally used the compounds arylazo-substituted at the coupling position of a colorless magenta coupler, which may include, for example, the compounds disclosed in U.S. Patents No. 2,801,171, No. 2,983,608, No. 3,005,712 and No. 3,684,514, British Patent No. 937,621, Japanese Unexamined Patent Publications No. 123625/1974 and No. 31448/1974.

The colored magenta couplers of the type such that a dye may flow out into a processing solution by the reaction with an oxidized product of a developing agent, as disclosed in U.S. Patent No. 3,419,391, can be also used.

As yellow couplers for photography, conventionally used are open-chain ketomethylene compounds, and there can be used benzoylacetanilide type yellow couplers and pivaroylacetanilide type couplers widely used in general. Two equivalent type yellow couplers wherein a carbon atom at the coupling position is substituted with a substituent eliminable through the coupling reaction can be also used. Examples of these, together with synthesis methods thereof, are disclosed in U.S. Patents No. 2,875,057, No. 3,265,506, No. 3,664,841, No. 3,408,194, No. 3,277,155, No. 3,447,928 and No. 3,415,652, Japanese Patent Publication No. 13576/1974, Japanese Unexamined Patent Publications No. 29432/1973, No. 68834/1973, No. 10736/1974, No. 122335/1974, No. 28834/1975 and No. 132926/1975, etc.

The above nondiffusion couplers in this invention may be used generally in an amount of 0.05 mole to 2.0 moles per mole of silver in the light-sensitive silver halide emulsion.

In this invention, besides the above nondiffusion couplers, a DIR compound may be preferably used.

Besides the DIR compound, a compound capable of releasing a development restrainer along with development may be also included in this invention, which may include, for example, the compounds disclosed in U.S. Patents No. 3,297,445 and No. 3,379,529, West German Patent Publication (OLS) No. 24 17 914, Japanese Unexamined Patent Publications No. 15271/1977, No. 9116/1978, No. 123838/1984 and No. 127038/1984, etc.

The DIR compound used in this invention is a compound capable of releasing a development restrainer through the reaction with an oxidized product of a color developing agent.

Such a DIR compound may typically include DIR couplers wherein a group capable of forming a compound having a development restraining action has been introduced to a coupler active site when eliminated from the active site, which are disclosed, for example, in

British Patent No. 935,454, U.S. Patents No. 3,227,554, No. 4,095,984 and No. 4,149,886, etc.

The above DIR couplers have a property that a coupler mother nucleus may form a dye and, on the other hand, a developing restrainer is released when coupled with an oxidized product of a color developing agent. In this invention, also included is such a compound capable of releasing a development restrainer but not forming any dye when coupled 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, Japanese Unexamined Patent Publications No. 110529/1978, No. 13333/1979 and No. 161237/1980, etc.

Still also included in this invention is the so-called timing DIR compound which is a compound such that a mother nucleus may form a dye or colorless compound when reacted with an oxidized product of a color developing agent, and on the other hand, an eliminated timing group may release a development restrainer through the intramolecular nucleophilic substitutive reaction or elimination reaction. As disclosed in Japanese Unexamined Patent Publication Nos. 145135/1979, 114946/1979 and 154234/1982.

There may be also included a timing DIR compound wherein the timing group as mentioned above has been attached onto a coupler mother nucleus capable of forming a perfectly diffusing dye when reacted with an oxidized product of a color developing agent, as disclosed in Japanese Unexamined Patent Publications No 160954/1983 and No. 162949/1983.

The DIR compound contained in the light-sensitive material may be used preferably in an amount ranging between 1×10^{-4} mole to 10×10^{-1} mole per mole of silver.

The light-sensitive silver halide color

photographic material used in this invention may additionally contain a variety of additives for photography. For example, there may be used antifoggants, stabilizers, ultraviolet absorbent, color stain preventive agents, brightening agents, color image-fading preventive agents, antistatic agents, hardening agents, surface active agents, plasticizers, wetting agents, etc. which are disclosed in Research Disclosure No. 17643.

In the light-sensitive silver halide color photographic material of this invention, hydrophilic colloid used for preparing an emulsion may include any of proteins such as gelatin, derived gelatin, graft polymers of gelatin with other macromolecules, albumin and casein; cellulose derivatives such as hydroxyethyl cellulose derivatives and carboxymethyl cellulose; starch derivatives; synthetic hydrophilic macromolecules of homopolymers or copolymers such as polyvinyl alcohol, polyvinyl imidazole and polyacrylamide; etc.

Supports for the light-sensitive silver halide color photographic material used in this invention may include, for example, baryta paper, polyethylene-coated paper, polypropylene synthetic paper, transparent supports provided with a reflection layer in combination, or using a reflecting body in combination, for example, glass plates, polyester films of cellulose acetate, cellulose nitrate or polyethylene terephthalate, polyamide films, polycarbonate films, polystyrene films, etc., and may also include other conventional transparent supports. These supports may be selected depending on what the light-sensitive materials are used for.

For applying the silver halide emulsion layers and other photographic constituent layers used in this invention, various coating methods can be used, including dip coating, air doctor coating, curtain coating, hopper coating, etc. A coating method of simultaneously applying two or more layers can be also used, according to the method disclosed in U.S. Patents No. 2,761,791 and No. 2,941,898.

In this invention, the respective emulsion layers may be applied in any positional order arbitrarily determined. For example, in the case of light-sensitive materials for full color photographic paper, it is preferred to arrange a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer in this order from the support side. These light-sensitive silver halide emulsion layers may each comprise two or more layers.

In the light-sensitive material of this invention, an intermediate layer or layers with appropriate thickness may be optionally provided depending on the purpose, and various layers such as a filter layer, an anticurl layer, a protective layer and an antihalation layer can be also used in appropriate combination as constituent layers. In these constituent layers, the above hydrophilic colloid that can be used in emulsion layers can be similarly used as a binding material therefor, and also in the layers the above-mentioned various additives that can be contained in emulsion layers can be contained.

The method of processing a light-sensitive silver halide color photographic material of this invention can be applied to any light-sensitive silver halide color photographic materials such as color paper, color negative films, color positive films, color reversal films for slides, color reversal films for motion pictures, color reversal films for televisions, and reversal color paper, if the light-sensitive silver halide color photographic material is a light-sensitive material to be processed according to the so-called internal development system wherein couplers are contained in the light-sensitive material substantially containing the above silver chloride.

As described in the foregoing, the processing method of this invention has made it possible to provide a color developing soluiton for processing a light-sensitive silver halide color photographic material that can achieve excellent storage stability and excellent photographic performances for fog and maximum density, and is particularly feasible for rapid processing, and a method employing the same.

This invention will be described below more specifically by Examples, but embodiments of this invention are by no means limited to these.

Example 1

Color developing solutions each having the following composition were prepared.

(Color developing Solution)

Potassium chloride	1.0 g
Potassium sulfite	0.1 g
Preservative (described in Table 1)	10 g
Chelating agent (described in Table 1)	2.0 g
Color developing agent (Exemplary Compound (A-1))	5.5 g
Potassium carbonate	30 g

Made up to 1 liter by adding water, and adjusted to pH 10.15 with use of potassium hydroxide and sulfuric acid.

To each of the above color developing solutions, 4 ppm of a ferric ion, 2 ppm of a copper ion and 100 ppm of a calcium ion were added (added by dissolving $FeCl_3$, $CuSO_4 \cdot 6H_2O$ and $CaCl_2$, respectively), and the solutions were stored at 40°C in a glass container having an open top rate of 30 cm^2/lit.(i.e., having an air-contacting area of 30 cm^2 per 1 liter of the color developing solution) for two weeks. Appearances (coloring degrees) of the color developing solutions after two weeks were observed to obtain the results shown in Table 1.

Appearances of the solutions were evaluated by classifying into the following four stages.

+++ : A large amount of tar generated
++ : Black colored
+ : Turned brown (Considerably color-changed)
- : Little color-changed

Table 1

Developing solution No.	Preservative	Chelating agent	Appearance of the solution after two weeks
(Comparative) 1	None	None	+++
(Comparative) 2	None	Exemplary compound (II - 2)	+++
(Comparative) 3	Sulfates of hydroxylamine	None	++
(Comparative) 4	Sulfates of hydroxylamine	Exemplary compound (II - 2)	+
(Comparative) 5	Exemplary compound (I - 1)	None	+
(This invention) 6	Exemplary compound (I - 1)	Exemplary compound (II - 2)	-
(This invention) 7	Exemplary compound (I - 1)	Exemplary compound (III - 1)	-
(This invention) 8	Exemplary compound (I - 1)	Exemplary compound (III - 2)	-
(This invention) 9	Exemplary compound (I - 2)	Exemplary compound (II - 2)	-
(This invention) 10	Exemplary compound (I - 3)	Exemplary compound (II - 2)	-

As will be clear from the results shown in Table 1, in the cases where sulfates of hydroxylamine are added, color change or blackening has occurred, though somewhat different in appearance depending on whether a chelating agent is present or not, to show that the preservativity is poor. On the other hand, Table 1 clearly shows that, in the cases where the preservatives of this invention were added, the preservativity has been remarkably improved by virtue of the combination with a chelating agent.

Example 2

The following layers were provided by coating on paper supports laminated with polyethylene, successively in the order from the support side to produce samples of light-sensitive materials.

Layer 1: A layer containing 1.0 g/m^2 of gelatin, 0.40 g/m^2 (in terms of silver; ditto hereinafter) of a blue-sensitive silver halide emulsion and 1.0 x 10^{-3} mole/m^2 of the following yellow coupler (Y-1) dissolved in 0.50 g/m^2 of dioctyl phthalate.

Layer 2: An intermediate layer comprising 0.65 g/m^2 of gelatin.

Layer 3: A layer containing 1.20 g/m^2 of gelatin, 0.24 g/m^2 of a green-sensitive silver halide emulsion and 1.0 x 10^{-3} mole/m^2 of the following magenta coupler (M-1) dissolved in 0.25 g/m^2 of dioctyl phthalate.

Layer 4: An intermediate layer comprising 1.1 g/m^2 of gelatin.

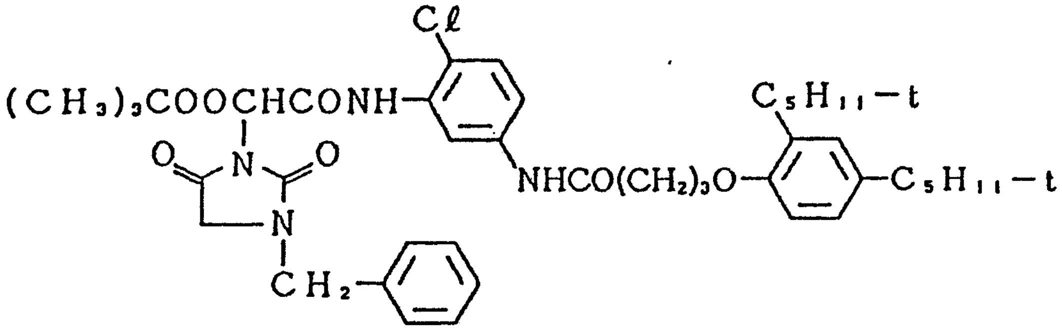
Layer 5: A layer containing 1.3 g/m^2 of gelatin, 0.27 g/m^2 of a red-sensitive silver halide emulsion and 1.75 x 10^{-3} mole/m^2 of the cyan coupler (C-76) mentioned above dissolved in 0.30 g/m^2 of dibutyl phthalate.

Layer 6: A layer containing 1.2 g/m^2 of gelatin and 0.30 g/m^2 of Tinuvin 328 (an ultraviolet absorbent produced by Ciba-Geigy Corp.) dissolved in 0.20 g/m^2 of dioctyl phthalate.

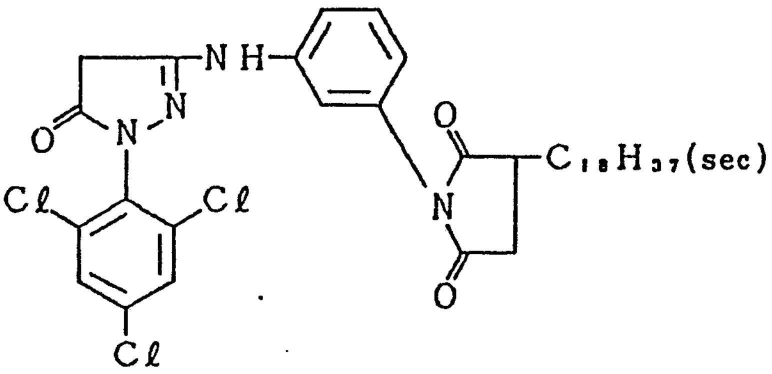
Layer 7: A layer containing 0.45 g/m^2 of gelatin.

As a hardening agent, 2,4-dichloro-6-hydroxy-s-triazine sodium salt was added to Layer 2, Layer 4 and Layer 7 each so as to be in an amount of 0.017 g per 1 g of gelatin.

Y-1



M-1



Silver halide compositions of respective silver halide emulsion are shown below in Table 2.

After carrying out wedgewise exposure on these samples according to a conventional method, the following developing was carried out.

Processing step	Processing temp.	Processing time
[1] Color developing	35°C	indicated in Table 2
[2] Bleach-fixing	35°C	45 sec.
[3] Washing	30°C	90 sec.
[4] Drying	60 to 80°C	60 sec.

Processing solutions used had the following composition.

[Color developing solution]

Potassium chloride	1.0 g
Potassium sulfite	0.25 g (2 x 10^{-3} mole)
Preservative (Exemplary Compound (I-1))	2.0 g
Chelating agent (Exemplary Compound (II-2))	1.0 g
Color developing agent (Exemplary Compound (A-1))	5.5 g
Potassium carbonate	30 g

Made up to 1 liter in total by adding water, and adjusted to pH 10.15 with use of potassium hydroxide or sulfuric acid.

[Bleach-fixing solution]

Ethylenediaminetetraacetic acid ferric ammonium dihydrate	60.0 g
Ethylenediaminetetraacetic acid	3.0 g
Ammonium thiosulfate (70% solution)	100.0 ml
Ammonium sulfite (40 % solution)	27.5 ml

Made up to 1 liter in total, and adjusted to pH 7.1 with use of potassium carbonate or glacial acetic acid.

Maximum reflection density of the yellow dye, obtained when color developing was carried out at 35°C for 10 minutes, was measured with use of an optical densitometer PDA-65 (produced by Konishiroku Photo Industry Co., Ltd. Here, the maximum reflection density of the the yellow dye was assumed as 100, and the developing time (developing completion time) necessary for the maximum reflection density of the yellow dye to be 80 is set forth in Table 2. This result is concerned with a developing completion time for the blue-sensitive emulsion layer having the slowest developing speed, thus showing the time in which the development of a light-sensitive material used has been completed.

Table 2

Sample No.	Silver haide composition (AgBr : AgCℓ) (molar ratio))			Developing completion time (second)
	Blue-sensitive layer	Green-sensitive layer	Red-sensitive layer	
1	25:75	25:75	25:75	128
2	22:78	22:78	22:78	123
3	20:80	20:80	20:80	91
4	15:85	15:85	15:85	75
5	10:90	10:90	10:90	62
6	5:95	5:95	5:95	47
7	5:95	2:98	2:98	45
8	2:98	2:98	2:98	43
9	2:98	100	100	40
10	100	100	100	37

As will be clear from Table 2, Samples No. 3 to No. 10 having 80 % or more of silver chloride content show that the developing completion time is short and they are feasible for rapid processing. In particular, it is understood that Samples No. 5 to No. 10 having 90 % or more of silver chloride content, especially, Samples No. 6 to 10 having 95 % or more of silver chloride content are particularly feasible for the rapid processing.

Example 3

Example 2 was repeated by using the same color developing solution as in Example 1 and the light-sensitive material as used in Example 2 (Sample No. 8) in accordance with the same procedural steps in Example 2, provided for using the color developing solution as used in Example 1 was left to stand for one week by an open top ratio of 10 cm^2/lit. and setting the color development time to 45 seconds.

After the processing, the minimum dessity and gamma value (tendency at a concentration of 0.3 to 0.8) of the cyan, magenta and yellow couplers were measured. As a result, there were found that the tendencies of the cyan, magenta and yellow couplers did not changed. The results are shown in Table 3.

Table 3

Sample No.	Processing solution No.	Storange period (40°C)	Yellow density	
			minimum density	gamma value
11 (Comparative)	1	None	0.04	2.86
12 (Comparative)	2	None	0.03	2.84
13 (Comparative)	3	None	0.03	0.95
14 (Comparative)	4	None	0.03	0.95
15 (Comparative)	5	None	0.03	2.85
16 (This invention)	6	None	0.03	2.85
17 (This invention)	7	None	0.03	2.86
18 (This invention)	8	None	0.03	2.85
19 (This invention)	9	None	0.03	2.82
20 (This invention)	10	None	0.03	2.86
21 (Comparative)	1	One week	0.20	2.01
22 (Comparative)	2	One week	0.14	2.22
23 (Comparative)	3	One week	0.16	0.98
24 (Comparative)	4	One week	0.12	1.16
25 (Comparative)	5	One week	0.09	2.92
26 (This invention)	6	One week	0.03	2.86
27 (This invention)	7	One week	0.03	2.89
28 (This invention)	8	One week	0.03	2.87
29 (This invention)	9	One week	0.03	2.84
30 (This invention)	10	One week	0.03	2.87

As will be clear from Table 3, in the case of using the processing soluiton of this invention, there are found that the minimum density and gamma value were changed little even after storage for one weeek at a temperature of 40 °C and that remarkable effects can be obtained as compared with the conventional hydroxylamine salts and that the processing solution of the present invention is preferred for rapid processing from the excellent gamma value.

Example 4

Using color paper samples used in Example 2, similar processing was repeated following the processing steps in Example 2 and using the processing solutions used in Example 2. However, the silver halide composition in the color paper samples was made to be 1 : 99 of AgBr : AgCl in the blue-sensitive emulsion layer, 5 : 95 in the green-sensitive emulsion layer, and 5 : 95 in the red-sensitive emulsion layer. Cyan couplers used were as shown in Table 4. Color developing processing time was 45 seconds. Concentration of potassium sulfite in the color developing solution was controlled as shown in Table 4. Chelating agents as shown in Table 4 were used in amount of 1.0 g/lit. The color developing solution used was obtained by adding 4 ppm of a ferric ion, 2 ppm of a copper ion and 1000 ppm of a calcium ion (added by dissolving $FeCl_3$, $CuSO_4 \cdot 6H_2O$ and $CaCl_2$, respectively), and stored for 5 days under the same conditions in Example 1. The maximum color density and minimum color density of the cyan dye after processing were measured to obtain the results shown in Table 4.

Table 4

Sample No.	Cyan coupler	Potassium sulfite	Chelating agent	Cyan density	
				minimun density	maximum density
31	Comparative 1	8.0×10^{-3}	None	0.15	2.26
32	Comparative 1	8.0×10^{-3}	Exemplary compound (II-2)	0.06	2.31
33	Comparative 2	8.0×10^{-3}	None	0.13	2.24
34	Comparative 2	8.0×10^{-3}	Exemplary compound (II-2)	0.04	2.28
35	Exemplary coupler C-76	8.0×10^{-3}	None	0.19	2.54
36	Exemplary coupler C-76	8.0×10^{-3}	Exemplary compound (II-2)	0.01	2.56
37	Exemplary coupler C-76	8.0×10^{-3}	Exemplary compound (II-3)	0.03	2.56
38	Exemplary coupler C-76	8.0×10^{-3}	Exemplary compound (II-1)	0.03	2.57
39	Exemplary coupler C-76	8.0×10^{-3}	Exemplary compound (II-2)	0.01	2.58
40	Exemplary coupler C-19	8.0×10^{-3}	Exemplary compound (II-2)	0.03	2.54
41	Exemplary coupler C-76 Exemplary coupler C-108	8.0×10^{-3}	Exemplary compound (II-2)	0.01	2.63

Table 4 (Cont'd)

Sample No.	Cyan coupler	Potassium sulfite	Chelating agent	Cyan density	
				minimun density	maximum density
42	Exemplary coupler C-76	2.0×10^{-3}	Exemplary compound (II-2)	0.02	2.67
43	Exemplary coupler C-76	4.0×10^{-3}	Exemplary compound (II-2)	0.01	2.61
44	Exemplary coupler C-76	2.0×10^{-2}	Exemplary compound (II-2)	0.01	2.54

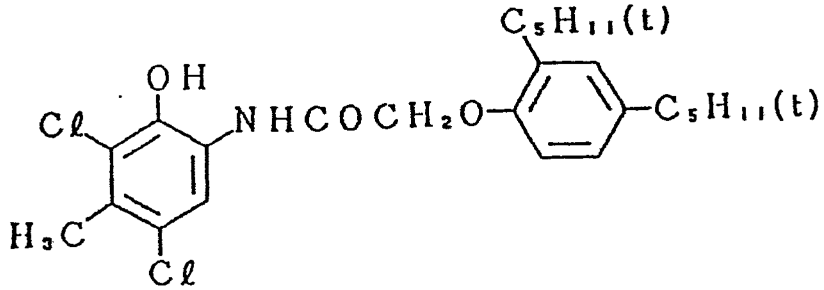
As will be clear from the results shown in Table 4, in the cases where the couplers outside this invention are used, there are shown disadvantages that the maximum color density of the cyan dye is greatly decreased and the minimum density is also high. On the other hand, in the cases where the cyan couplers of this invention are used, decrease in the maximum color density is little seen, but the minimum density is extremely high when no chelating agent is present. However, the results satisfying both the maximum color density and the minimum density were obtained by the combination of the coupler of this invention with the chelating agent of this invention.

In the samples of this invention, it was also possible to obtain still better maximum color density by lowering the concentration of sulfite.

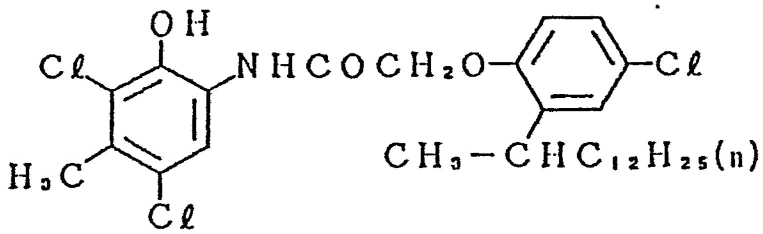
The same results as in the above were also obtained when Exemplary Compounds C-102, C-1, C-3 and C-58 were used as cyan couplers in Sample No. 38, and also when Exemplary Compounds II-1, II-4 to II-7 and III-2 to III-4 were used as chelating agents in Sample No. 36.

Comparative cyan couplers:

Comp. 1



Comp. 2



Example 5

Using the light-sensitive color photographic materials produced in Example 2 (silver halide composition is shown in Table 5), the following processing was carried out to evaluate silver-developing properties on the color developing solutions Nos. 2, 4 and 6 (containing no color developing agent).

Standard processing steps: (Processing temperature and processing time)

[1] Color developing	35°c	45 sec.
[2] Fixing	35°c	45 sec.
[3] Washing	30°c	90 sec.
[4] Drying	60 to 80°C	60 sec.

(Fixing solution)

Ammonium thiosulfate (70 % solution)	150.0 ml
Ammonium sulfite (40 % solution)	20 ml

Made up to 1 liter in total by adding water, and adjusted to pH 7.00 with used of ammonium hydroxide or acetic acid.

After developing processing, using PDA-65 (produced by Konishiroku Photo Industry Co., Ltd.), spectral reflection density was measured on the samples by orange light to evaluate D_{max} of the samples. Difference between the spectral reflection density for D_{max} and the spectral reflection density for D_{min} was assumed as a typical characteristic of silver density.

Results are shown in Table 5.

Table 5

Sample No.	Color developing solution No.	Silver halide composition (AgBr : AgCℓ) (molar ratio)			Reflection silver density
		Blue-sensitive layer	Green-sensitive layer	Red-sensitive layer	
45	2	25:75	25:75	25:75	0.00
46	2	20:80	20:80	20:80	0.00
47	2	15:85	15:85	15:85	0.00
48	2	10:90	10:90	10:90	0.00
49	2	5:95	5:95	5:90	0.00
50	2	2:98	2:98	2:98	0.00
51	2	0:100	0:100	0:100	0.00
52	4	25:75	25:75	25:75	0.06
53	4	20:80	20:80	20:80	0.20
54	4	15:85	15:85	15:85	0.30
55	4	10:90	10:90	10:90	0.39
56	4	5:95	5:95	5:95	0.45
57	4	2:98	2:98	2:98	0.49
58	4	0:100	0:100	0:100	0.56
59	6	25:75	25:75	25:75	0.00
60	6	20:80	20:80	20:80	0.01
61	6	15:85	15:85	15:85	0.01
62	6	10:90	10:90	10:90	0.02
63	6	5:95	5:95	5:95	0.03
64	6	2:98	2:98	2:98	0.03
65	6	0:100	0:100	0:100	0.04

As will be clear from Table 5, all of Samples No. 52 to No. 58 using hydroxylamine show high silver density and the silver development is seen to have proceeded. In particular, the silver development is seen to have proceeded in Samples No. 53 to No. 58 having 80 % or more of silver chloride content. However, in the color developing solution No. 6 employing Exemplary Compound I-1 of this invention, the silver development has little taken place regardless of the content of silver chloride.

Example 6

Using Samples 1, 3 and 6 used in Example 2 (provided that cyan couplers used are shown in Table 6), and also using the developing solution No. 6 used in Example 1 as a color developing solution (provided that potassium sulfite used is as shown in Table 6), the influence to the cyan density (maximum reflection density) by the silver halide composition and sulfite was examined.

Developing processing and evaluation method were in accordance with Example 2.

Results obtained are shown in Table 6.

Table 6

Sample No.	Silver halide composition (AgBr : AgCℓ) (molar ratio) (red-sensitive layer)	Potassium sulfite (mole/ℓ) of color developing solution	Cyan maximum density	
			Comparative coupler	coupler of this invention C - 76
66	Sample No. 1 used in Example (2) 25:75	4.0×10^{-2}	2.25	2.30
67	Sample No. 1 used in Example (2) 25:75	1.0×10^{-2}	2.29	2.32
68	Sample No. 1 used in Example (2) 25:75	4.0×10^{-3}	2.34	2.35
69	Sample No. 1 used in Example (2) 25:75	1.0×10^{-3}	2.35	2.36
70	Sample No. 3 used in Example (2) 20:80	4.0×10^{-2}	2.12	2.40
71	Sample No. 3 used in Example (2) 20:80	1.0×10^{-2}	2.35	2.47
72	Sample No. 3 used in Example (2) 20.80	4.0×10^{-3}	2.48	2.50
73	Sample No. 3 used in Example (2) 20:80	1.0×10^{-3}	2.50	2.53
74	Sample No. 6 used in Example (2) 5:95	4.0×10^{-2}	2.19	2.50
75	Sample No. 6 used in Example (2) 5.95	1.0×10^{-2}	2.39	2.54
76	Sample No. 6 used in Example (2) 5.95	4.0×10^{-3}	2.57	2.58
77	Sample No. 6 used in Example (2) 5.95	1.0×10^{-3}	2.59	2.60

As will be clear from Table 6, in the cases where the silver chloride as the silver halide composition is in Samples No. 66 to No. 69, the developing time is so short as to give lower cyan density, but is not so greatly affected by the density of potassium sulfite or the type of cyan couplers. On the other hand, in the Samples No. 70 to No. 77, the cyan density is high even with shorter developing time because of higher developing speed when 80 mole % or more of silver chloride is used, but, when couplers other than those of this invention are used, the density is greatly dependent on the amount of potassium sulfite. The decrease in density is particularly remarkable when 1.0×10^{-2} or more of potassium sulfite is present, but, in the cases where the couplers of this invention are used, it is seen that the cyan density decreases only a little, and further that very good maximum density can be obtained when the concentration of sulfite is 4.0×10^{-3} or less.

Example 7

The following layers were provided by coating on paper supports laminated with polyethylene, successively in the order from the support side to produce samples of light-sensitive materials.

Layer 1: A layer containing 1.0 g/m^2 of gelatin, 0.38 g/m^2 (in terms of silver; ditto hereinafter) of a blue-sensitive silver halide emulsion and 1.0×10^{-3} mole/m^2 of the yellow coupler (Y-1) used in Example 1, dissolved in 0.50 g/m^2 of dioctyl phthalate.

Layer 2: An intermediate layer comprising 0.65 g/m^2 of gelatin.

Layer 3: A layer containing 1.15 g/m^2 of gelatin, 0.25 g/m^2 of a green-sensitive silver halide emulsion and 1.0×10^{-3} mole/m^2 of the magenta coupler (M-1) used in Example 1, dissolved in 0.25 g/m^2 of dioctyl phthalate.

Layer 4: An intermediate layer comprising 1.1 g/m^2 of gelatin.

Layer 5: A layer containing 1.3 g/m^2 of gelatin, 0.28 g/m^2 of a red-sensitive silver halide emulsion and 1.75 x 10^{-3} mole/m^2 of the cyan coupler (C-108) dissolved in 0.25 g/m^2 of dibutyl phthalate.

Layer 6: A layer containing 1.0 g/m^2 of gelatin and 0.31 g/m^2 of Tinuvin 328 (an ultraviolet absorbent produced by Ciba-Geigy Corp.) dissolved in 0.20 g/m^2 of dioctyl phthalate.

Layer 7: A layer containing 0.48 g/m^2 of gelatin.

As a hardening agent, 2,4-dichloro-6-hydroxy-s-triazine sodium salt was added to Layer 2, Layer 4 and Layer 7 each so as to be in an amount of 0.017 g per 1 g of gelatin.

The silver halide composition in each of the silver halide emulsions is shown in Table 7.

On these samples, processing was applied in the following manner:

Processing step	Processing temp.	Processing time
[1] Color developing	35°c	45 sec.
[2] Bleach-fixing	35°c	45 sec.
[3] Washing	30°c	90 sec.
[4] Drying	60 to 80°C	60 sec.

Processing solutions used had the following composition.

[Color developing solution]

Potassium chloride	1.0 g
Potassium sulfite	0.25 g (2 x 10^{-3} mole)
Preservative (Exemplary Compound (I-1))	10.0 g
Chelating agent (Exemplary Compound (II-2))	1.0 g
Color developing agent (Exemplary Compound (A-1))	5.5 g
Potassium carbonate	30 g

Made up to 1 liter in total by adding water, and adjusted to pH 10.15 with use of potassium hydroxide or sulfuric acid.

[Bleach-fixing solution]

Ethylenediaminetetraacetic acid ferric ammonium dihydrate	60.0 g
Ethylenediaminetetraacetic acid	3.0 g
Ammonium thiosulfate (70% solution)	100.0 ml
Ammonium sulfite (40 % solution)	27.5 ml

Made up to 1 liter in total, and adjusted to pH 7.1 with use of potassium carbonate or glacial acetic acid.

Maximum reflection density of the yellow dye, obtained when color developing was carried out at 35°C for 10 minutes, was measured with use of an optical densitometer PDA-65 (produced by Konishiroku Photo Industry Co., Ltd. Here, the maximum reflection density of the the yellow dye was assumed as 100, and the developing time (developing completion time) necessary for the maximum reflection density of the yellow dye to be 80 is set forth in Table 7. This result is concerned with a developing completion time for the blue-sensitive emulsion layer having the slowest developing speed, thus showing the time in which the development of a light-sensitive material used has been completed.

Table 7

Sample No.	Silver halide composition (AgBr : AgCℓ) (molar ratio)			Developing completion time (second)
	Blue-sensitive layer	Green-sensitive layer	Red-sensitive layer	
78	25 : 75	25 : 75	25 : 75	125
79	22 : 78	22 : 78	22 : 78	120
80	20 : 80	20 : 80	20 : 80	90
81	15 : 85	15 : 85	15 : 85	75
82	10 : 90	10 : 90	10 : 90	60
83	5 : 95	5 : 95	5 : 95	48
84	5 : 95	2 : 98	2 : 98	45
85	2 : 98	2 : 98	2 : 98	42
86	2 : 98	100	100	39
87	100	100	100	35

As will be clear from Table 7, Samples No. 80 to No. 87 having 80 % or more of silver chloride content show that the developing completion time is short and they are feasible for rapid processing. In particular, it is understood that Samples No. 82 to No. 87 having 90 % or more of silver chloride content, especially, Samples No. 83 to 87 having 95 % or more of silver chloride content are particularly feasible for the rapid processing.

Example 8

Using color paper samples used in Example 7, similar processing was repeated following the processing steps in Example 7 and using the processing solutions used in Example 7. However, the silver halide composition in the color paper samples was made to be 3 : 97 of AgBr : AgCl in the blue-sensitive emulsion layer, 3 : 97 in the green-sensitive emulsion layer, and 1 : 99 in the red-sensitive emulsion layer. Cyan couplers used were as shown in Table 8. Color developing processing time was 45 seconds. Concentration of potassium sulfite in the color developing solution was controlled as shown in Table 8. Chelating agents as shown in Table 8 were used in amount of 1.0 g/lit. The color developing solution used was obtained by adding 4 ppm of a ferric ion, 2 ppm of a copper ion and 100 ppm of a calcium ion (added by dissolving $FeCl_3$, $CuSO_4 \cdot 6H_2O$ and $CaCl_2$, respectively), and stored for 5 days under the same conditions in Example 1. The maximum color density and minimum color density of the cyan dye after processing were measured to obtain the results shown in Table 8.

Table 8

Sample No.	Cyan coupler	Potassium sulfite mole/ℓ of color developing solution	Chelating agent	Cyan density	
				minimun density	maximum density
88	Comparative 1	8.0×10^{-3}	None	0.14	2.26
89	Comparative 1	8.0×10^{-3}	Exemplary compound (II-2)	0.05	2.32
90	Comparative 2	8.0×10^{-3}	None	0.12	2.27
91	Comparative 2	8.0×10^{-3}	Exemplary compound (III-2)	0.14	2.30
92	Exemplary coupler C-108	8.0×10^{-3}	None	0.21	2.56
93	Exemplary coupler C-108	8.0×10^{-3}	Exemplary compound (II-2)	0.01	2.58
94	Exemplary coupler C-108	8.0×10^{-3}	Exemplary compound (II-3)	0.02	2.58
95	Exemplary coupler C-108	8.0×10^{-3}	Exemplary compound (III-1)	0.02	2.57
96	Exemplary coupler C-108	8.0×10^{-3}	Exemplary compound (III-5)	0.01	2.59
97	Exemplary coupler C-102	8.0×10^{-3}	Exemplary compound (II-2)	0.03	2.53
98	Exemplary coupler C-104	8.0×10^{-3}	Exemplary compound (II-2)	0.02	2.54

Table 8 (Cont'd)

Sample No.	Cyan coupler	Potassium sulfite mole/ℓ of color developing solution	Chelating agent	Cyan density	
				minimun density	maximum density
99	Exemplary coupler C-108	2.0×10^{-3}	Exemplary compound (II-2)	0.02	2.69
100	Exemplary coupler C-108	4.0×10^{-3}	Exemplary compound (II-2)	0.01	2.63
101	Exemplary coupler C-108	2.0×10^{-2}	Exemplary compound (II-2)	0.01	2.53

As will be clear from the results shown in Table 8, in the cases where the couplers outside this invention are used, there are shown disadvantages that the maximum color density of the cyan dye is greatly decreased and the minimum density is also high. On the other hand, in the cases where the cyan couplers of this invention are used, decrease in the maximum color density is little seen, but the minimum density is extremely high when no chelating agent is present. However, the results satisfying both the maximum color density and the minimum density were obtained by the combination of the coupler of this invention with the chelating agent of this invention.

In the samples of this invention, it was also possible to obtain still better maximum color density by lowering the concentration of sulfite.

The same results as in the above were also obtained when Exemplary Compounds C-109 and C-128 were used as cyan couplers in Sample No. 95, and also when Exemplary Compounds II-1, II-4 to II-6 and III-2 to III-4 were used as chelating agents in Sample No. 93.

Example 9

Using the light-sensitive color photographic materials produced in Example 7 (silver halide composition is shown in Table 9), the following processing was carried out to evaluate silver-developing properties on the color developing solutions Nos. 2, 4 and 6.

Standard processing steps: (Processing temperature and processing time)

[1] Color developing	35°C	45 sec.
[2] Fixing	35°C	45 sec.
[3] Washing	30°C	90 sec.
[4] Drying	60 to 80°C	60 sec.

(Bleach-fixing solution)

Ammonium thiosulfate (79 % solution)	150.0 ml

Ammonium sulfite (40 % solution)	20 ml

Made up to 1 liter in total by adding water, and adjusted to pH 7.00 with used of ammonium hydroxide or acetic acid.

After developing processing, using PDA-65 (produced by Konishiroku Photo Industry Co., Ltd.), spectral reflection density was measured on the samples by orange light to evaluate D_{max} of the samples. Difference between the spectral reflection density for D_{max} and the spectral reflection density for D_{min} was assumed as a typical characteristics of silver density.

Results obtained are shown in Table 9.

Table 9

Sample No.	Color developing solution	Silver halide composition (AgBr : AgCℓ) (molar ratio)			Reflection silver density
		Blue-sensitive layer	Green-sensitive layer	Red-sensitive layer	
102	2	25 : 75	25 : 75	25 : 75	0.00
103	2	20 : 80	20 : 80	20 : 80	0.00
104	2	15 : 85	15 : 85	15 : 85	0.00
105	2	10 : 90	10 : 90	10 : 90	0.00
106	2	5 : 95	5 : 95	5 : 95	0.00
107	2	2 : 98	2 : 98	2 : 98	0.00
108	2	0 : 100	0 : 100	0 : 100	0.00
109	4	25 : 75	25 : 75	25 : 75	0.05
110	4	20 : 80	20 : 80	20 : 80	0.18
111	4	15 : 85	15 : 85	15 : 85	0.27
112	4	10 : 90	10 : 90	10 : 90	0.36
113	4	5 : 95	5 : 95	5 : 95	0.41
114	4	2 : 98	2 : 98	2 : 98	0.43
115	4	0 : 100	0 : 100	0 : 100	0.52
116	6	25 : 75	25 : 75	25 : 75	0.00
117	6	20 : 80	20 : 80	20 : 80	0.01
118	6	15 : 85	15 : 85	15 : 85	0.01
119	6	10 : 90	10 : 90	10 : 90	0.02
120	6	5 : 95	5 : 95	5 : 95	0.02
121	6	2 : 98	2 : 98	2 : 98	0.02
122	6	0 : 100	0 : 100	0 : 100	0.03

As will be clear from Table 9, all of Samples No. 109 to No. 115 using hydroxylamine show high silver density and the silver development is seen to have proceeded. In particular, the silver development is seen to have proceeded in Samples No. 110 to No. 115 having 80 % or more of silver chloride content.

However, in the color developing solution No. 26 employing Exemplary Compound I-1 of this invention, the silver development has little taken place regardless of the content of silver chloride.

Example 10

Using Samples 78, 80 and 83 used in Example 7 (provided that cyan couplers used are shown in Table 10), and also using the developing solution No. 6 used in Example 1 as a color developing solution (provided that potassium sulfite used is as shown in Table 10), the influence to the cyan density (maximum reflection density) by the silver halide composition and sulfite was examined. Developing processing and evaluation method were in accordance with Example 7.

Results obtained are shown in Table 10.

Table 10

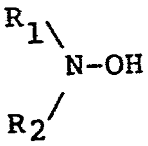
Sample No.	Silver halide composition (AgBr : AgCℓ) (molar ratio) (red-sensitive layer)	Potassium sulfite (mole/ℓ) of color developing solution	Cyan maximum density	
			Comparative coupler	coupler of this invention C - 108
123	Sample No. 58 used in Example (7) 25:75	$4.0\text{x}10^{-2}$	2.27	2.33
124	Sample No. 58 used in Example (7) 25:75	$1.0\text{x}10^{-2}$	2.30	2.36
125	Sample No. 58 used in Example (7) 25:75	$4.0\text{x}10^{-3}$	2.34	2.37
126	Sample No. 58 used in Example (7) 25:75	$1.0\text{x}10^{-3}$	2.36	2.37
127	Sample No. 60 used in Example (7) 20:80	$4.0\text{x}10^{-2}$	2.14	2.41
128	Sample No. 60 used in Example (7) 20:80	$1.0\text{x}10^{-2}$	2.36	2.49
129	Sample No. 60 used in Example (7) 20:80	$4.0\text{x}10^{-3}$	2.52	2.54
130	Sample No. 60 used in Example (7) 20:80	$1.0\text{x}10^{-3}$	2.57	2.56
131	Sample No. 63 used in Example (7) 5:95	$4.0\text{x}10^{-2}$	2.18	2.51
132	Sample No. 63 used in Example (7) 5:95	$1.0\text{x}10^{-2}$	2.43	2.56
133	Sample No. 63 used in Example (7) 5:95	$4.0\text{x}10^{-3}$	2.61	2.56
134	Sample No. 63 used in Example (7) 5:95	$1.0\text{x}10^{-3}$	2.65	2.65

As will be clear from Table 10, in the cases where the silver chloride as the silver halide composition is in Samples No. 123 to No. 126), the developing time is so short as to give lower cyan density, but is not so greatly affected by the density of potassium sulfite or the type of cyan couplers. On the other hand, in Samples No. 127 to No. 134), the cyan density is high even with shorter developing time because of higher developing speed when 80 mole % or more of silver chloride is used, but, when couplers other than those of this invention are used, the density is greatly dependent on the amount of potassium sulfite. The decrease in density is particularly remarkable when 1.0×10^{-2} or more of potassium sulfite is present, but, in the cases where the couplers of this invention are used, it is seen that the cyan density decreases only a little, and further that very good maximum density can be obtained when the concentration of sulfite is 4.0×10^{-3} or less.

Claims:

1. A color developing solution for processing a light-sensitive silver halide color photographic material, which comprises the compound represented by General Formula (I) shown below and at least one selected from the group consisting of the compounds represented by General Formula (II) and (III) shown below:

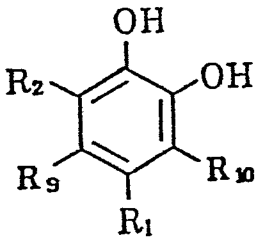
General Formula (I)



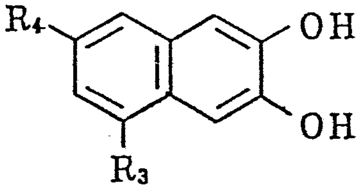
$$\begin{matrix} R_1 \diagdown \\ \quad N\text{-}OH \\ R_2 \diagup \end{matrix}$$

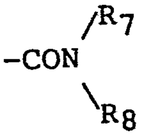
wherein R_1 and R_2 each represent an alkyl group having 1 to 3 carbon atoms,

General Formula (II)



General Formula (III)

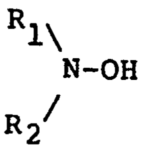


wherein, in Formulas (II) and (III), R_1, R_2, R_3, R_4, R_9 and R_{10} each represent a hydrogen atom, a halogen atom, a sulfonic acid group, an alkyl group having 1 to 7 carbon atoms, $-OR_5$, $-COOR_6$,  $-CON\begin{matrix} \diagup R_7 \\ \diagdown R_8 \end{matrix}$, or a phenyl group, wherein R_5, R_6, R_7 and R_8 each represent a hydrogen atom or an alkyl group having 1 to 18 carbon atoms.

2. The color developing solution according to Claim 1, wherein further comprises color developing agent including p-phenylenediamine type compounds having a water soluble group.

3. A method of processing a light-sensitive silver halide color photographic material having at least one silver halide emulsion layer, which comprises, after imagewise exposure of a light-sensitive silver halide color photographic material, carrying out processing including at least a color developing step, wherein said processing is carried out by use of a color developing solution comprising the compound represented by General Formula (I) shown below and at least one selected from the group consisting of the compounds represented by General Formula (II) and (III) shown below:

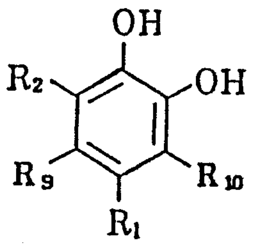
General Formula (I)



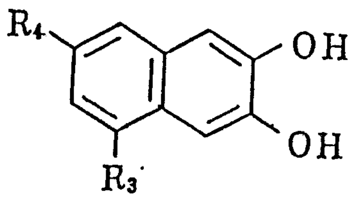
$$\begin{matrix} R_1\diagdown \\ \quad N\text{-}OH \\ R_2\diagup \end{matrix}$$

wherein R_1 and R_2 each represent an alkyl group having 1 to 3 carbon atoms,

General Formula (II)



General Formula (III)



wherein, in Formulas (II) and (III), R_1, R_2, R_3, R_4, R_9 and R_{10} each represent a hydrogen atom, a halogen atom, a sulfonic acid group, an alkyl group having 1 to 7 carbon atoms, $-OR_5$, $-COOR_6$,

$$-CON\begin{matrix}/R_7\\ \backslash R_8\end{matrix}$$

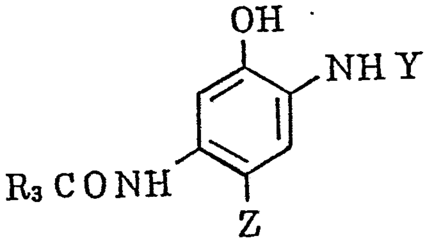
, or a phenyl group,

wherein R_5, R_6, R_7 and R_8 each represent a hydrogen atom or an alkyl group having 1 to 18 carbon atoms.

4. The method of processing a light-sensitive silver halide color photographic material according to Claim 3, wherein said silver halide emulsion layer contains silver halide grins comprised of 80 mol% of silver chloride.

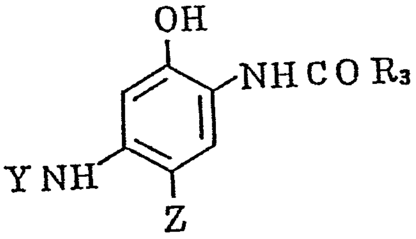
5. The method of processing a light-sensitive silver halide color photographic material according to Claim 3, wherein at least one layer of said silver halide emulsion layers contains at least one cyan coupler selected from the group consisting of the cyan couplers represented by the following general formulas (C-I) and (C-II):

General Formula (C-I)

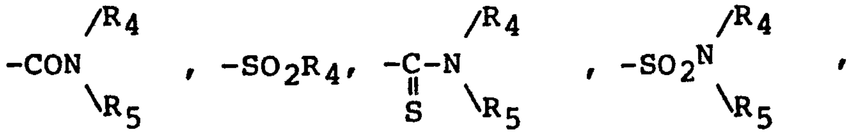


,

General Formula (C-II)



wherein Y represents $-COR_4$,

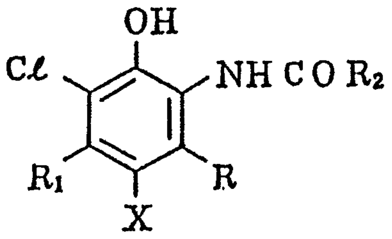


$$-CON\begin{matrix}/R_4\\ \backslash R_5\end{matrix},\ -SO_2R_4,\ -\underset{\underset{S}{\|}}{C}-N\begin{matrix}/R_4\\ \backslash R_5\end{matrix},\ -SO_2N\begin{matrix}/R_4\\ \backslash R_5\end{matrix},$$

$-CONHCOR_4$ or $-CONHSO_2R_4$, wherein R_4 represents an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, a heterocyclic group, R_5 represents a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or a heterocyclic group, and R_4 and R_5 may be combined each other to form a 5- or 6-membered ring; R_3 represents a ballast group; and Z represents a hydrogen atom or a group eliminatable through the coupling reaction with an oxidized product of an aromatic primary amine color developing agent.

6. The method of processing a light-sensitive silver halide color photographic material according to Claim 3, wherein at least one layer of said silver halide emulsion layers contains a cyan coupler represented by the following general formula (C-III):

General Formula (C-III)



wherein one of R and R_1 represents a hydrogen atom and the other of them represents a straight chain or branched alkyl group having 2 to 12 carbon atoms; X represents a hydrogen atom or a group eliminable through the coupling reaction with an oxidized product of a N-hydroxyalkyl substituted-p-phenylenediamine derivative color developing agent; and R_2 represents a ballast group.