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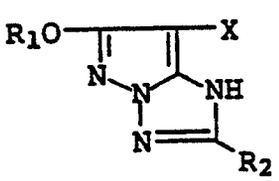
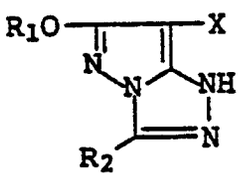
(54) Color photographic light-sensitive material.

(57) A silver halide color photographic material which contains at least one coupler represented by the general formula (I) or (II-A) and at least one compound represented by the following general formula (III) in the same light-sensitive silver halide layer:



(I)



(II-A)

wherein R_1 represents an alkyl group, an aryl group, or a heterocyclic group; R_2 represents a hydrogen atom, or a substituent group; and X represents a hydrogen atom, or a coupling-off group.

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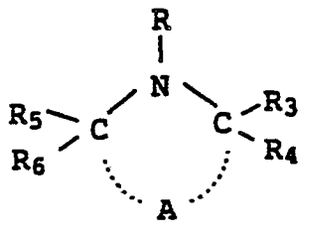


(III)

wherein R represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an oxy radical, or a hydroxyl group; R_3, R_4, R_5 and R_6, which may be the same or different, each represents a hydrogen atom, or an alkyl group; and A represents a nonmetallic atomic group necessary for forming a 5-, 6- or 7-membered ring; provided that R_3 may be linked with R_4, R_5 may be linked with R_6, R may be linked with R_3, or R_3 may be linked with A to form a 5 or 6-membered ring.

COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide color photographic material, and, more particularly, to a light-sensitive material which has excellent color reproducibility and high color developability, and shows a considerably suppressed increase in density of the unexposed part after photographic processing.

BACKGROUND OF THE INVENTION

Color images are well known to be formed by reacting couplers with oxidized color developing agents of primary amine type, which have been oxidized using optically exposed silver halides as an oxidizing agent, to produce indophenol, indoaniline, indamine, azomethine, phenoxazine, phenazine and their analogous dyes.

In order to form magenta color images, couplers of 5-pyrazolone, cyanoacetophenone, indazolone, pyrazolobenzimidazole and pyrazolotriazole types have been employed.

Most of the magenta color image-forming couplers which have been studied and widely used up to the present are 5-pyrazolones. However, dyes produced from 5-pyrazolone type couplers show an undesired absorption having a yellow component in the neighborhood of 430 nm, which is responsible for color turbidity.

As the nuclei of magenta color image-forming couplers which reduce of the aforesaid yellow component, there have been proposed pyrazolobenzimidazole nuclei in British Patent 1,047,612, indazolone nuclei in U.S. Patent 3,770,447, and pyrazolo[5,1-c]-1,2,4-triazole nuclei in U.S. Patent 3,725,067.

However, magenta couplers disclosed in the above-cited patents remain unsatisfactory. For instance, when these couplers are mixed with a silver halide emulsion dispersed in a hydrophilic protective colloid like gelatin, color images produced therefrom are unsatisfactory; their solubilities in high boiling organic solvents are low; they are difficult to synthesize; they have no more than comparatively low coupling activities in ordinary developers; and dyes produced therefrom have extremely low fastness to light.

As a result of searching for magenta couplers without subsidiary absorption in the neighborhood of 430 nm, which is the most serious defect of 5-pyrazolone type couplers in respect of hue, the present inventors found that 1H-pyrazolo[1,5-b]-1,2,4-triazole type magenta couplers showed no subsidiary absorption in the short wavelength region, produced color images of high fastness and were synthesized with ease, and disclosed them in JP-A-59-171956 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and U.S. Patent 4,540,654. These couplers further have advantages in that they are excellent in color reproducibility and synthesizing facility, and can be converted to two-equivalent couplers by introducing a splitting-off group to the coupling active site, to reduce the amount of silver to be used.

However, these couplers had low color developability, and the photographic properties of the magenta images produced therefrom were greatly changed with fluctuation in concentrations of ingredients contained in processing baths (e.g., sulfite ion and a hydroxylamine derivative added to a developer as an oxidation inhibitor for a color developing agent) under running processing.

As a means for overcoming these defects, introduction of an alkyloxy group or an aryloxy group in the 6-position of the foregoing 1H-pyrazolo[1,5 b]-1,2,4-triazole type magenta couplers has been disclosed in JP-A-62-209457. Though successful in enhancing color developability and considerably depressing the changes in photographic properties under running processing, this coupler had a problem of the generation of stain (increase in density of unexposed areas) with the lapse of time after photographic processing.

Stains caused in a silver halide color photographic material are undesirable, since that they not only degrade the quality of white areas of the image but also aggravate the turbidity in colored areas of the image and spoil the visual sharpness of the image. In particular, the reflection density of stains in reflex materials (e.g., color paper) is, in theory, emphasized several times over the transmission density. Therefore, only slight stains spoil the image quality to result in a serious problem. Although the incorporation of the compounds described in JP-A-62-96944 and JP-A-62-92945 into sensitive materials was disclosed for the purpose of suppressing the generation of stains, those compounds still cannot produce

sufficient effects upon the couplers in question.

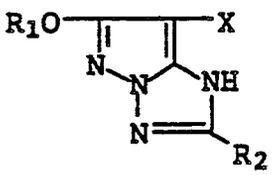
On the other hand, the art of using hindered amines and pyrazolotriazole type couplers in combination is disclosed in European Patent 218,266. However, the patent does not have any examples in which the pyrazolotriazole type couplers substituted by an alkyloxy group, an aryloxy group or a heterocyclyl group at the 6-position are used. Therefore, it is not easy to analogize the effects of the present invention from the above-cited patent.

Under these circumstances, a new method of lessening the influences of fluctuation in processing conditions and depressing the increase of stain is greatly desired.

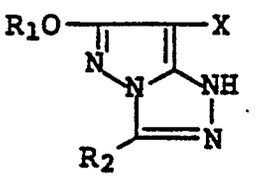
SUMMARY OF THE INVENTION

An object of the present invention is to provide a light-sensitive material which has sufficiently high color developability and excellent color reproducibility, and without an increase in density of the unexposed part with the lapse of time.

It has now been found that this and other objects of the present invention is attained with a silver halide color photographic material which contains at least one coupler represented by the following general formula (I) or (II-A), and at least one compound represented by the following general formula (III) in the same layer:

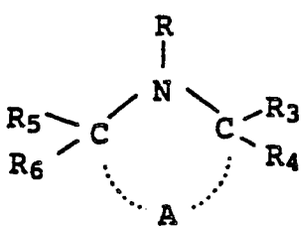


(I)



(II-A)

wherein R_1 represents an alkyl group, an aryl group, or a heterocyclic group; R_2 represents a hydrogen atom, or a substituent group; and X represents a hydrogen atom, or a coupling-off group.

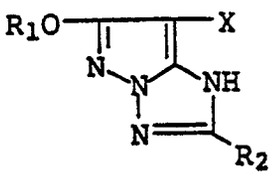


(III)

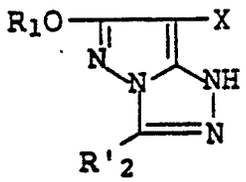
wherein R represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an oxy radical, or a hydroxyl group; R_3, R_4, R_5 and R_6, which may be the same or different, each represents a hydrogen atom or an alkyl group; and A represents a nonmetalic atomic group necessary for forming a 5-, 6- or 7-membered ring; provided that R_3 may be linked with R_4, R_5 may be linked with R_6, R may be linked with R_3, or R_3 may be linked with A to form a 5- or 6-membered ring.

DETAILED DESCRIPTION OF THE INVENTION

It is preferred that at least one light-sensitive silver halide layer contains at least one coupler represented by formula (I) or (II-B) in combination with at least one compound represented by formula (III) above:



(I)



(II-B)

wherein R_1 represents an alkyl group, an aryl group or a heterocyclic group; R_2 represents hydrogen, a halogen, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, an acylamino group, an anilino group, a ureido group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, or an alkoxycarbonyl group; X represents hydrogen or a coupling-off group; when R_1 represents an alkyl group, R'_2 represents an alkyl group, an aryl group, an alkylthio group, an arylthio group or a heterocyclic thio group; and when R_1 represents an aryl group or a heterocyclic group, R'_2 represents hydrogen or an alkyl group, an aryl group, an alkylthio group, an arylthio group or a heterocyclic thio group, an alkoxycarbonyl group, a sulfinyl group, or a carbonyl group.

The magenta couplers represented by the foregoing general formulae (I) and (II-A) are described in detail below.

R_1 represents a substituted or unsubstituted alkyl group such as methyl, ethyl, isopropyl, t-butyl, trifluoromethyl, phenylmethyl, methoxyethyl, 2-phenoxyethyl, 2-methylsulfonylethyl, 2-hydroxyethyl, 3,3,3-trifluoropropyl, 2-fluoroethyl, 2-chloroethyl, 2-bromoethyl, 2-cyanoethyl, 3-oxobutyl, or 3-oxobutyl; a substituted or unsubstituted aryl group such as phenyl, 4-methylphenyl, 4-t-butylphenyl, 4-acylaminophenyl, 4-halogenophenyl, or 4-alkoxyphenyl; or a substituted or unsubstituted heterocyclic group such as 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl, 2-pyridyl, or 4-pyridyl; a phenyl group substituted by an alkoxy group at the ortho position is preferred.

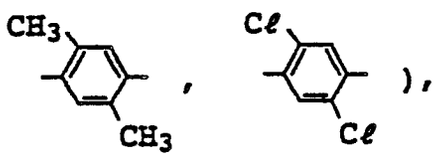
R_2 represents hydrogen, a halogen atom (e.g., chlorine, bromine); a substituted alkyl group, such as a sulfonamido-substituted alkyl group (e.g., sulfonamidomethyl, 1-sulfonamidoethyl, 2-sulfonamidoethyl, 1-methyl-2-sulfonamidoethyl, 3-sulfonamidopropyl), an acylamino-substituted alkyl group (e.g., acylaminomethyl, 1-acylaminoethyl, 2-acylaminoethyl, 1-methyl-2-acylaminoethyl, 3-acylaminopropyl), a sulfonamido-substituted phenylalkyl group (e.g., p-sulfonamidophenylmethyl, p-sulfonamidophenylethyl, 1-(p-sulfonamidophenyl)ethyl, p-sulfonamidophenylpropyl), an acylamino-substituted phenylalkyl group (e.g., p-acylamino phenylmethyl, p-acylaminophenylethyl, 1-(p-acylaminophenyl)ethyl, p-acylaminophenylpropyl), an alkylsulfonyl-substituted alkyl group (e.g., 2-dodecylsulfonylethyl, 1-methyl-2-pentadecylsulfonylethyl, octadecylsulfonylpropyl), or a phenylsulfonyl-substituted alkyl group (e.g., 3-(2-butyl-5-t-octylphenylsulfonyl)propyl, 2-(4 dodecyloxyphenylsulfonyl)ethyl); an unsubstituted alkyl group (e.g., methyl, ethyl, hexyl, dodecyl); an aryl group (e.g., a substituted aryl group such as sulfonamidophenyl, acylaminophenyl, alkoxyphenyl, aryloxyphenyl, substituted alkylphenyl, sulfonamidonaphthyl, or acylaminonaphthyl and an unsubstituted aryl group such as phenyl, and naphthyl); a heterocyclic group (e.g., 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl); a cyano group; an alkoxy group (e.g., methoxy, ethoxy, 2-methoxyethoxy, 2-dodecylethoxy, 2-methanesulfonylethoxy); an aryloxy group (e.g., phenoxy, 2-methylphenoxy, 4-t-butylphenoxy); an acylamino (e.g., acetamido, benzamido, tetradecanamido, α-(2,4-di-t-amylphenoxy)butylamido, γ-(3-t-butyl-4-hydroxyphenoxy)butylamido, α-[4-(4-hydroxyphenylsulfonyl)phenoxy]decanamido); an anilino group (e.g., phenylamino, 2-chloroanilino, 2-chloro-5-tetradecanamidoanilino, 2-chloro-5-dodecyloxycarbonylanilino, N-acetylanilino, 2-chloro-5-[α-(3-t-butyl-4-hydroxyphenoxy)dodecanamido]anilino); a ureido group (e.g., phenylureido, methylureido, N,N-dibutylureido); a sulfamoylamino group (e.g., N,N-dipropylsulfamoylamino, N-methyl-N-decylsulfamoylamino); an alkylthio group (e.g., methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio, 3-(4-t-butylphenoxy)propylthio); an arylthio group (e.g., phenylthio, 2-butoxy-5-t-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio, 4-tetradecanamidophenylthio); an alkoxycarbonylamino group (e.g., methoxycarbonylamino, tetradecyloxycarbonylamino); a sulfonamido group (e.g., methanesulfonamido, hexadecanesulfonamido, benzenesulfonamido, p-toluenesulfonamido, octadecanesulfonamido, 2-methyloxy-5-t-butylbenzenesulfonamido); a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl, N-(2-dodecyloxyethyl)carbamoyl, N-methyl-N-dodecylcarbamoyl, N-[3-(2,4-di-t-amylphenoxy)propyl]carbamoyl); a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-(2-dodecyloxyethyl)sulfamoyl, N-ethyl-N-dodecylsulfamoyl, N,N-diethylsulfamoyl); a sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl, toluenesulfonyl); or an alkoxycarbonyl group (e.g., methoxycarbonyl, butyloxycarbonyl, dodecylcarbonyl, octadecylcarbonyl). Of these groups, an alkyl group, an aryl group, an alkylthio group and an arylthio group are preferred as R_2. In

particular, an alkyl group and an aryl group are more preferred.

In particular, when the couplers are represented by the general formula (II-A), and therein R_1 represents an alkyl group, it is desirable that R_2 represents an alkyl group, an aryl group, an alkylthio group, an arylthio group, a heterocyclicthio group, an alkoxycarbonyl group, a sulfinyl group or a carbamoyl group.

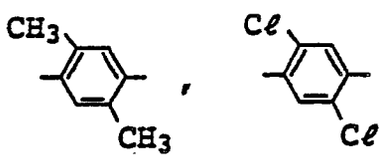
X represents hydrogen or a coupling-off group, e.g., a halogen atom (e.g., chlorine, bromine, iodine); a carboxyl group; a group connected to the coupling active site via an oxygen atom (e.g., acetoxy, propanoyloxy, benzoyloxy, 2,4-dichlorobenzoyloxy, ethoxyoxaloyloxy, pyruvinyloxy, cinnamoyloxy, phenoxy, 4-cyanophenoxy, 4-methanesulfonamidophenoxy, 4-methanesulfonylphenoxy, α-naphthoxy, 3-pentadecylphenoxy, benzyloxycarbonyloxy, ethoxy, 2-cyanoethoxy, benzyloxy, 2-phenethyloxy, 2-phenoxyethoxy, 5-phenyltetrazolyloxy, 2-benzothiazolyloxy); a group connected to the coupling active site via a nitrogen atom (e.g., benzenesulfonamido, N-ethyltoluenesulfonamido, heptafluorobutanamido, 2,3,4,5,6-pentafluorobenzamido, octanesulfonamido, p-cyanophenylureido, N,N-diethylsulfamoylamino, 1-pyperidyl, 5,5-dimethyl-2,4-dioxo-3-oxazolidinyl, 1-benzyl-ethoxy-3-hydantoinyl, 2N-1,1- dioxo-3(2H)-oxo-1,2-benzoisothiazolyl, 2-oxo-1,2-dihydro-1-pyridinyl, imidazolyl, pyrazolyl, 3,5-diethyl-1,2,4-triazol-1-yl, 5- or 6-bromobenzotriazol-1-yl, 5-methyl-1,2,3,4-tetrazol-1-yl, benzimidazolyl); or a group connected to the coupling active site via a sulfur atom (e.g., phenylthio, 2-carboxyphenylthio, 2-methoxy-5-t-octylphenylthio, 4-methanesulfonylphenylthio, 4-octanesulfonamidophenylthio, benzylthio, 2-cyanoethylthio, 1-ethoxycarbonyltridecylthio, 5-phenyl-2,3,4,5-tetrazolylthio, 2-benzothiazolyl). Preferably, the coupling-off group is connected to the coupling active site by a sulfur atom.

R_1, R_2, or X may be a divalent group via which the magenta coupler of formula (I) or (II-A) forms a bis compound, R_1 or R_2 represents a substituted or unsubstituted alkylene group (e.g., methylene, ethylene, 1,10-decylene, $-CH_2CH_2-O-CH_2CH_2-$), or a substituted or unsubstituted phenylene group (e.g., 1,4-phenylene, 1,3-phenylene,

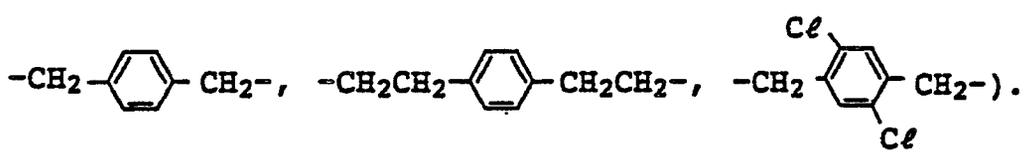


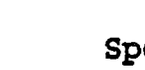
while X represents a divalent group derived from any of the above-cited monovalent groups.

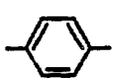
When the moiety represented by formula (I) or (II-A) is contained in a vinyl monomer, a linkage group represented by R_1 or R_2 includes those formed by combining two or more divalent groups selected from among substituted or unsubstituted alkylene groups (e.g., methylene, ethylene, 1,10-decylene, $-CH_2CH_2OCH_2CH_2-$), substituted or unsubstituted phenylene groups (e.g., 1,4-phenylene, 1,3-phenylene,

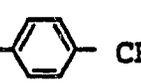

), -NHCO-, -CONH-, -O-, -OCO-, and

substituted or unsubstituted aralkylene groups (e.g.,



Specifically, $-CH_2CH_2-$, $-CH_2CH_2CH_2$  $-NHCO-$,

 $-NHCO-$, $-CH_2CH_2NHCO-$, $-CH_2CH_2OCO-$,

$-CH_2CH_2OCH_2CH_2NHCO-$, and $-CH_2CH_2$  CH_2CH_2NHCO- are

preferred as the combined linkage group.

The vinyl group in such a vinyl monomer may contain a substituent group in addition to the moiety represented by formula (I) or (II-A). Preferred substituent groups include hydrogen, chlorine, or a lower alkyl group having from 1 to 4 carbon atoms (e.g., methyl, ethyl).

The monomer containing the coupler moiety represented by the general formula (I) or (II-A) may form a copolymer together with an ethylenically unsaturated monomer incapable of undergoing a coupling reaction with the oxidation product of an aromatic primary amine developing agent, and therefore, which cannot produce a color.

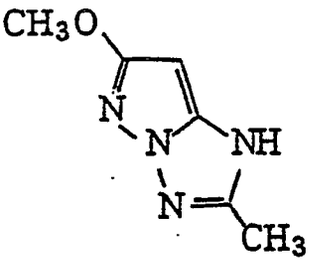
Specific examples of such non-color-producing ethylenically unsaturated monomers include acrylic acid, α-chloroacrylic acid, α-alkylacrylic acid (e.g., methacrylic acid), and esters or amides derived from these acrylic acids (e.g., acrylamide, n-butylacrylamide, t-butylacrylamide, diacetone acrylamide, methacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, iso-butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, β-hydroxymethacrylate), methylenedibisacrylamide, vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (e.g., styrene and derivatives thereof, vinyltoluene, divinyl benzene, vinylacetophenone, sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers (e.g., vinyl ethyl ether), maleic acid, maleic anhydride, maleic acid esters, N-vinyl-2-pyrrolidone, N-vinylpyridine, and 2- and 4-vinylpyridine. Two or more non-color-producing ethylenically unsaturated monomers can be used together. For example, a combination of n-butyl acrylate with methyl acrylate, of styrene with methacrylic acid, of methacrylic acid with acrylamide, and of methyl acrylate with diacetone acrylamide can be used.

As is well-known in the field of polymer color couplers, non-color-producing ethylenically unsaturated monomers to be copolymerized with a solid water-insoluble coupler monomer can be selected so as to produce desirable physical and/or chemical properties of the resulting copolymers, for example, solubility, compatibility with a binder (such as gelatin) contained in a photographic colloidal composition, flexibility, thermal stability, and so on.

Polymer couplers to be used in the present invention may be either soluble or insoluble in water, and are particularly preferably in the form of a latex.

Specific examples of representative magenta couplers to be used in the present invention are illustrated below. However, the invention is not to be construed as being limited to these examples. Addition ally, all ratios herein of constitutional repeating units of polymer couplers are by weight.

(1)



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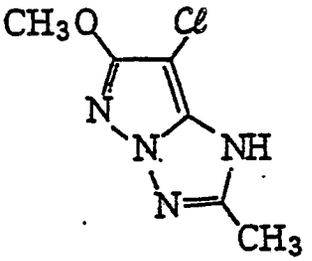

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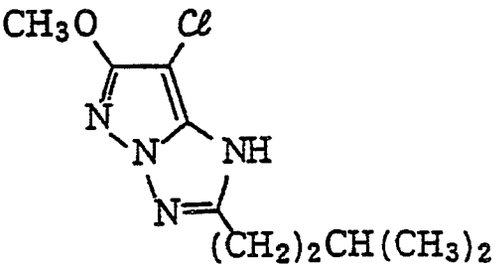

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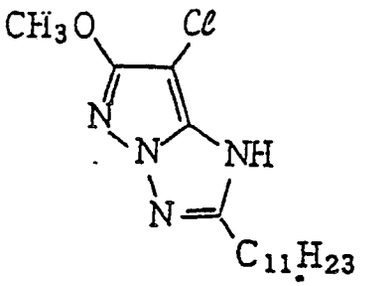

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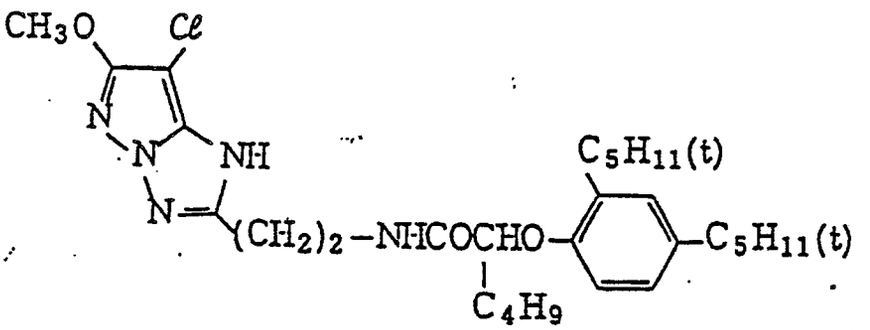

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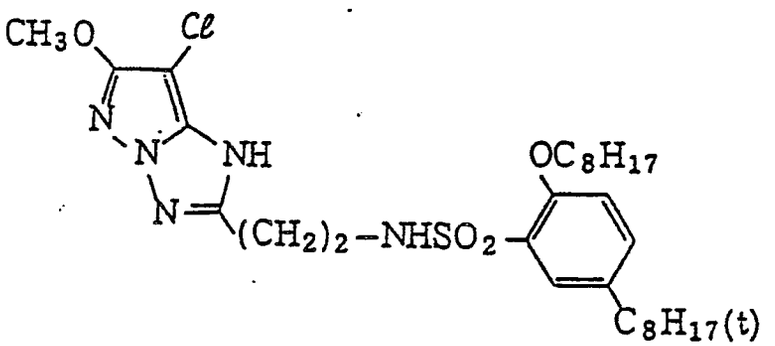

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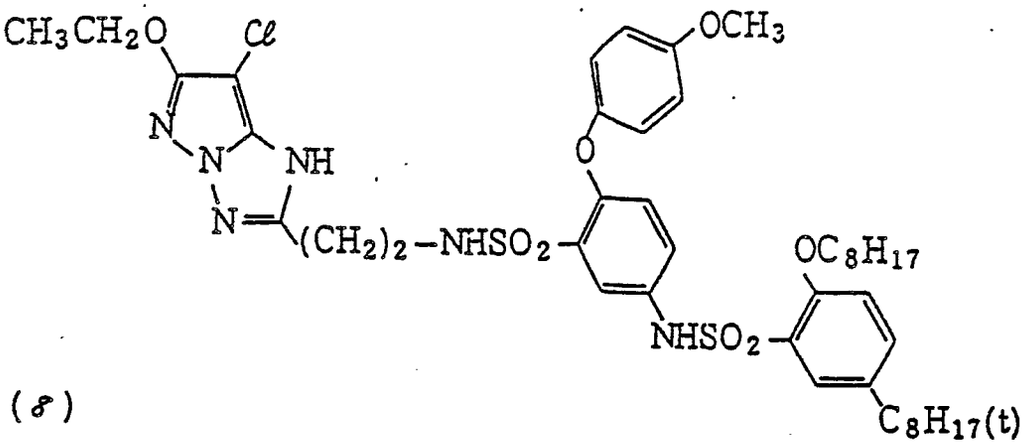

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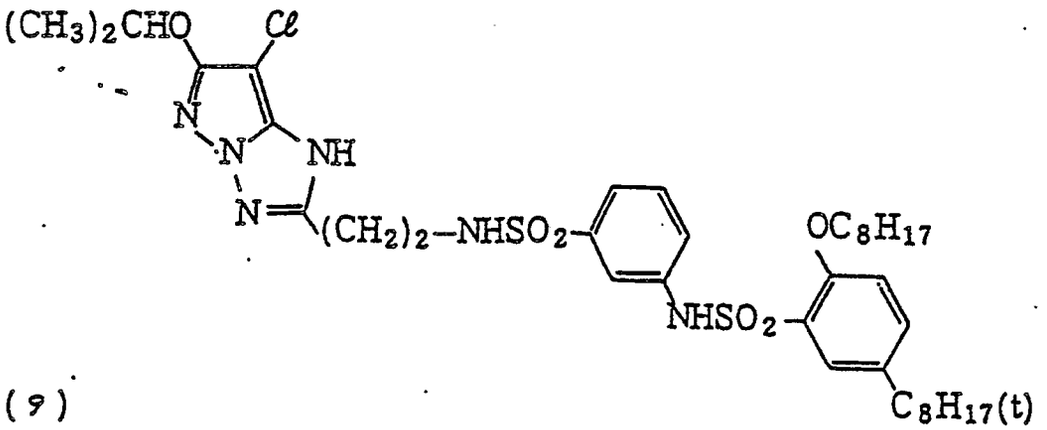

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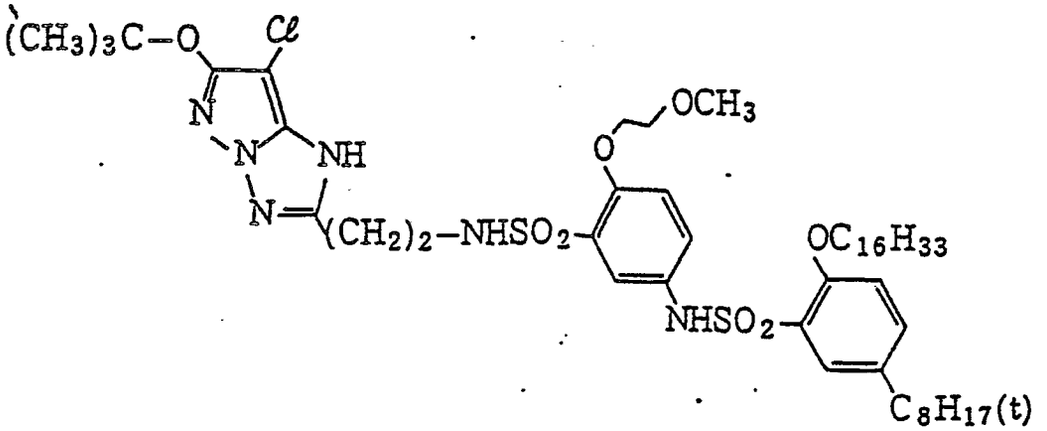

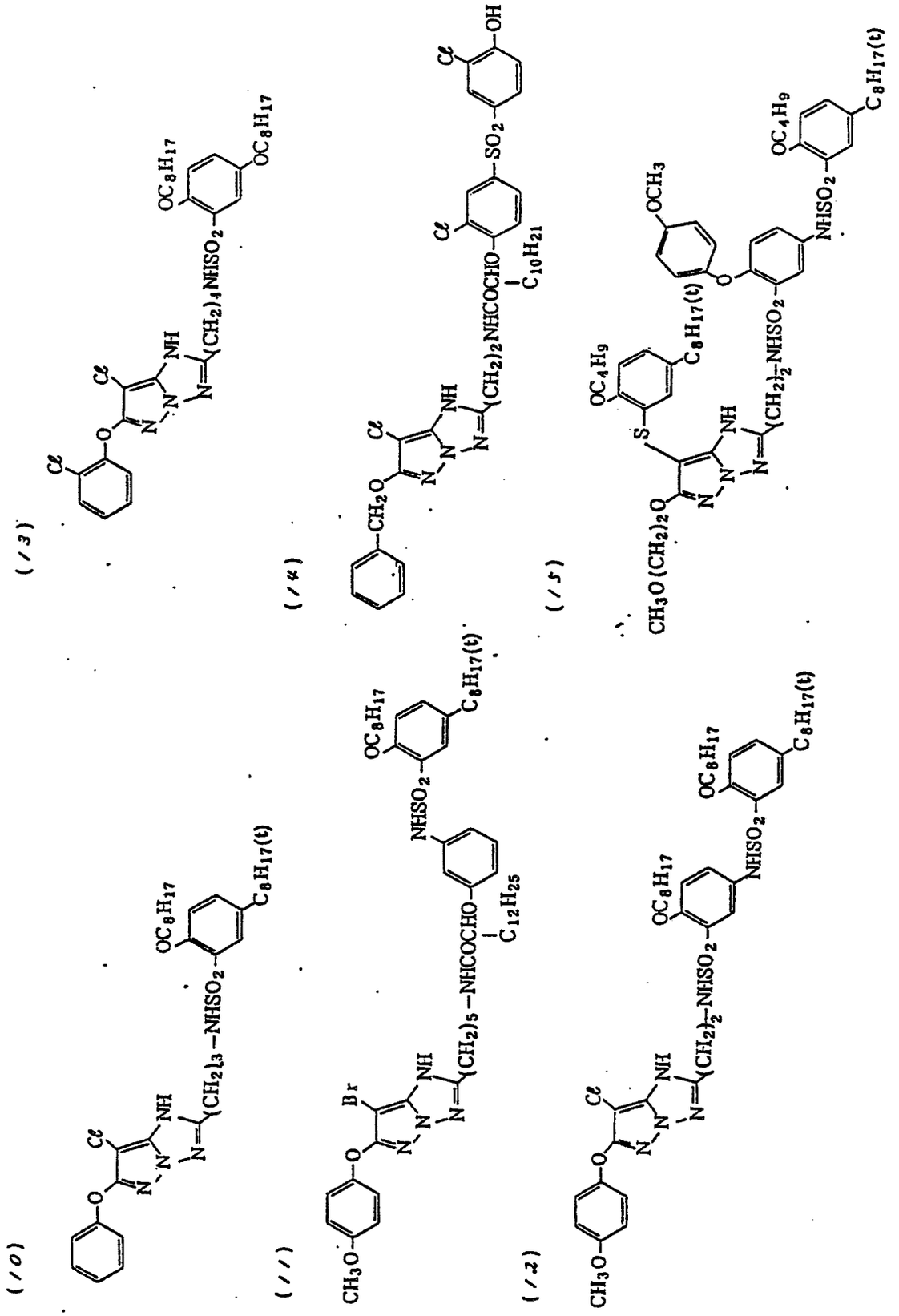

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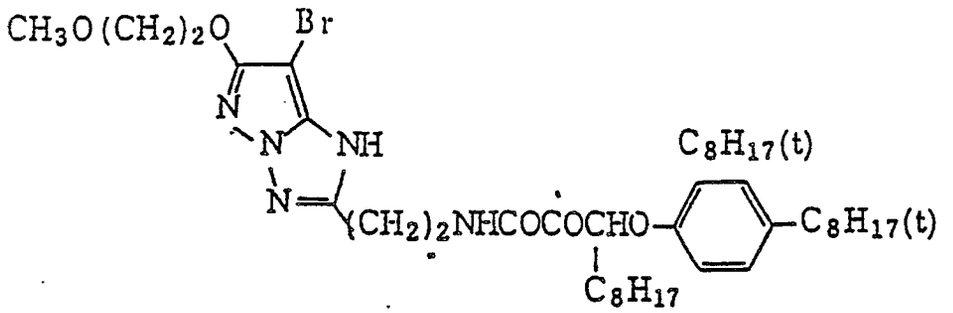

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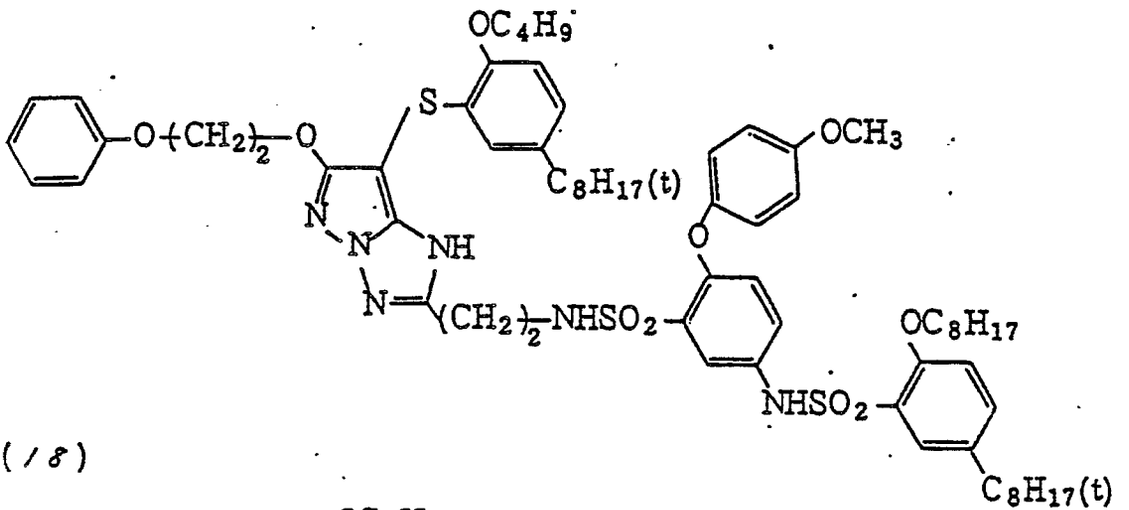

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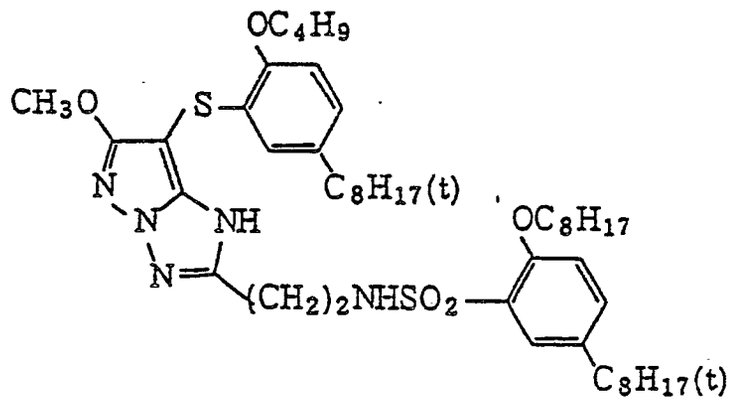

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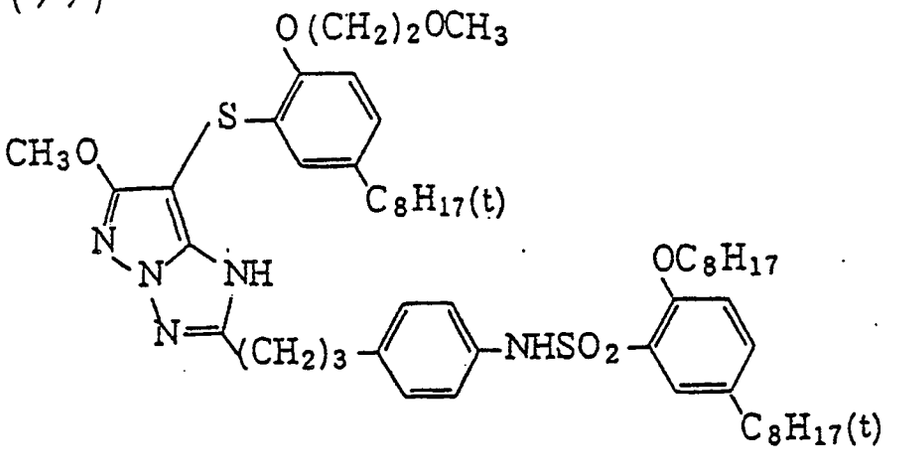

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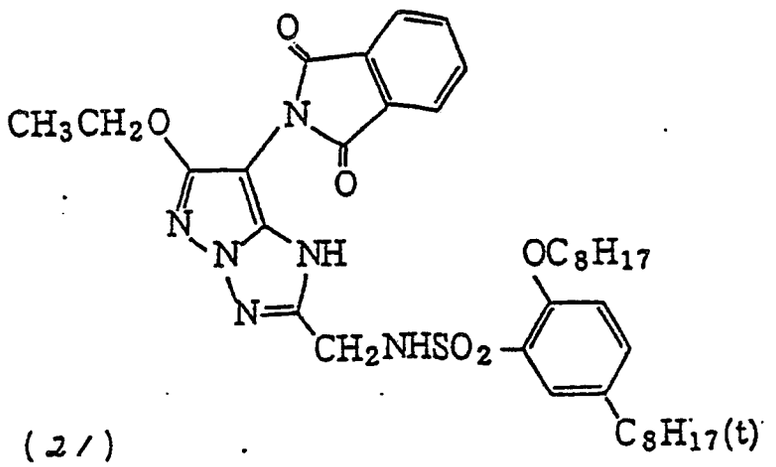

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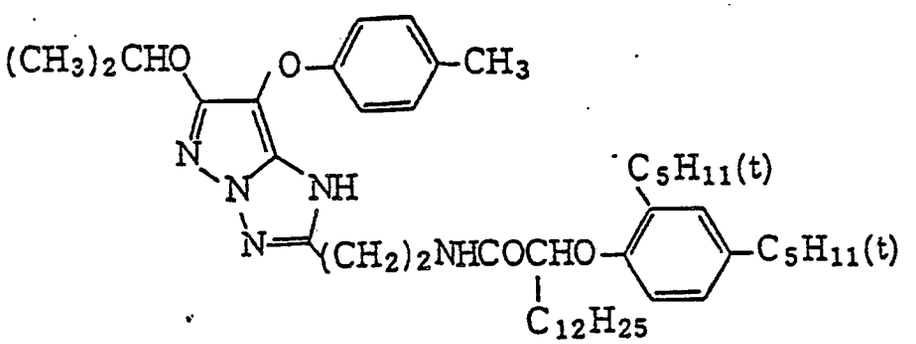

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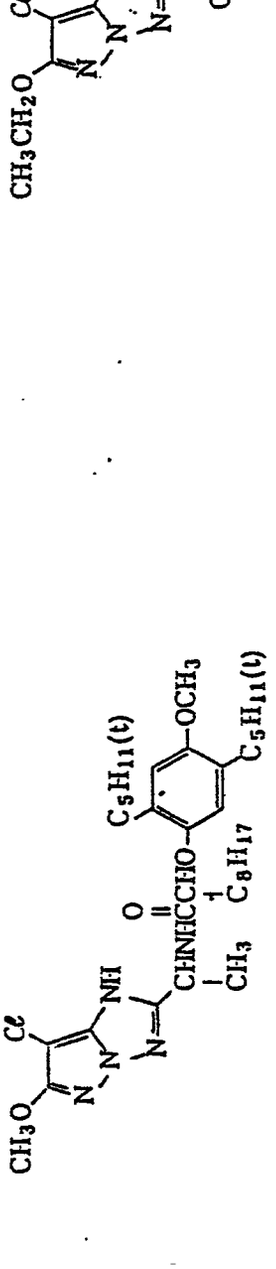

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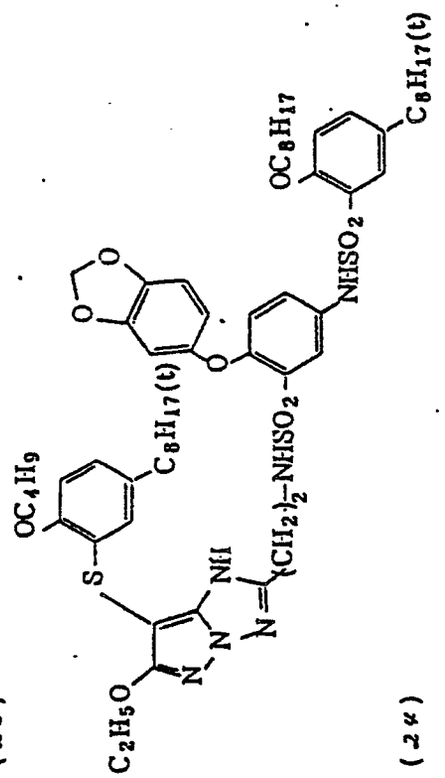

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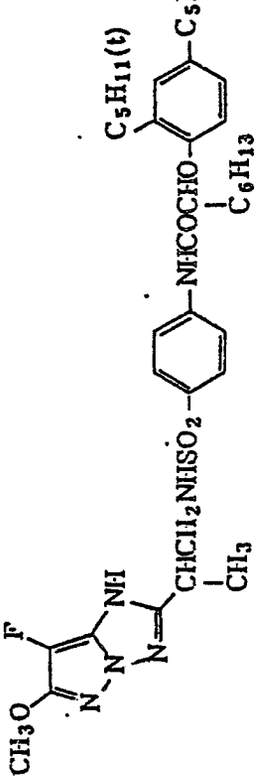

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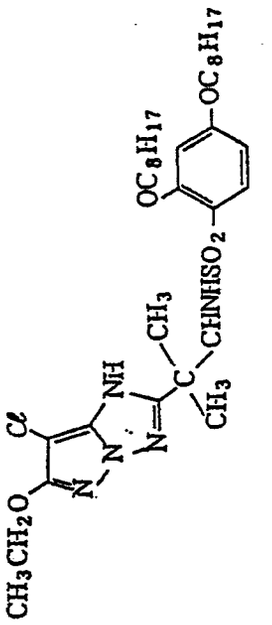

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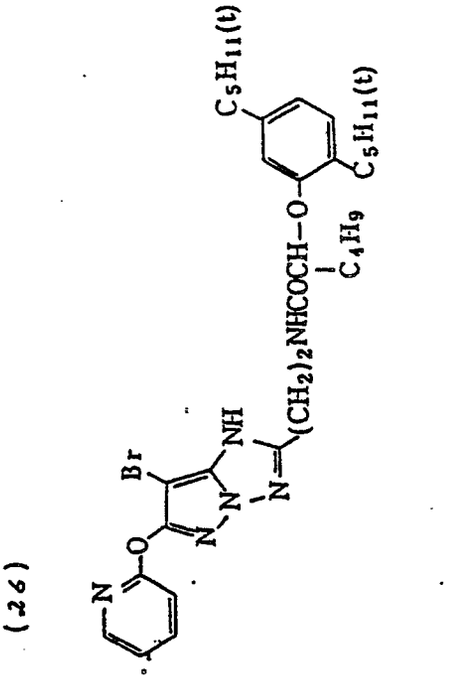

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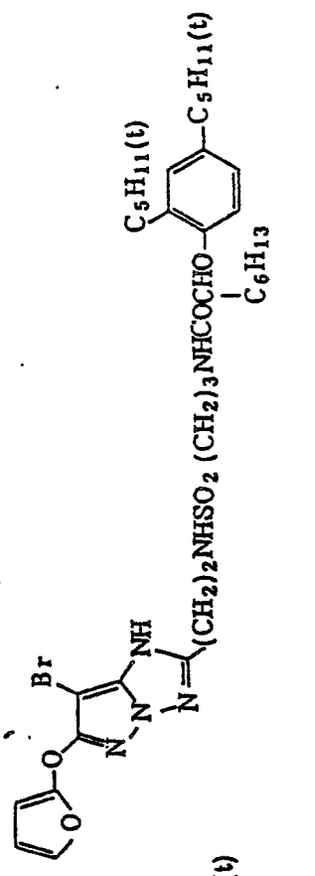

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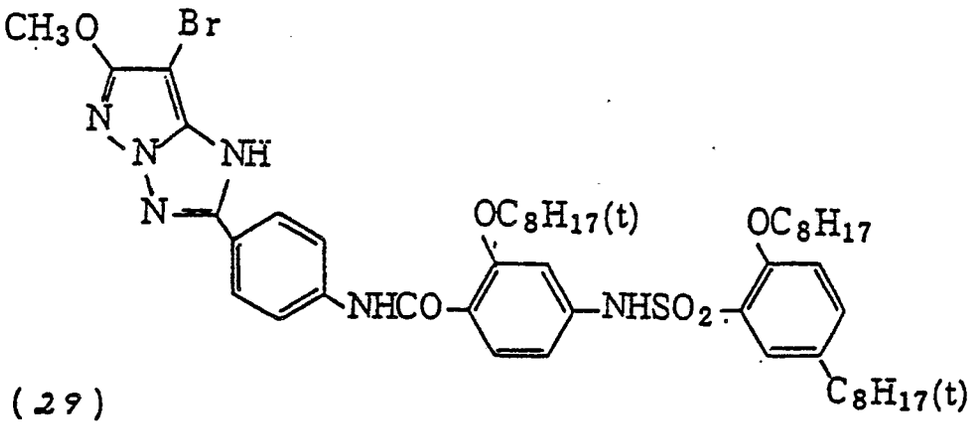

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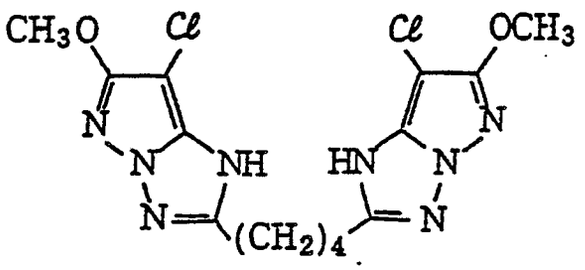

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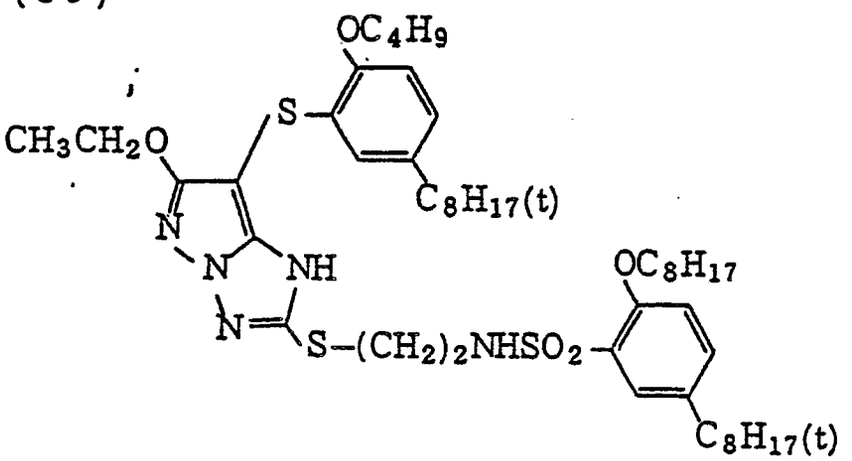

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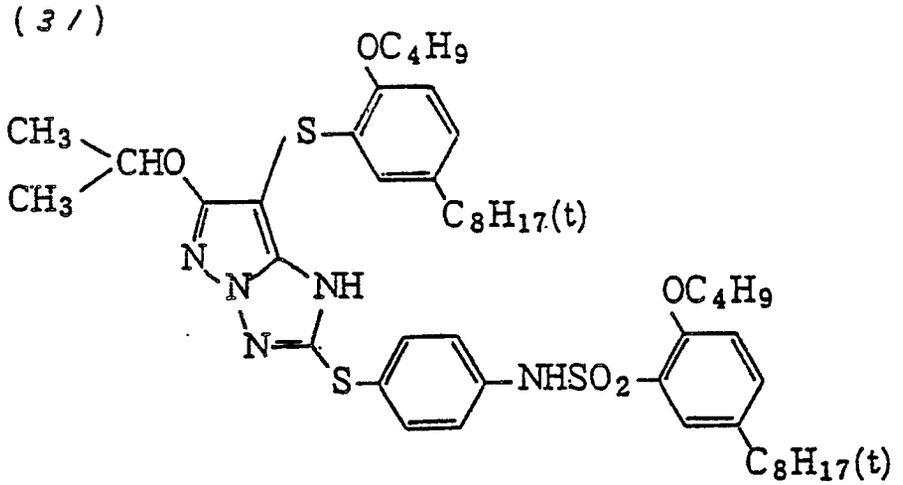

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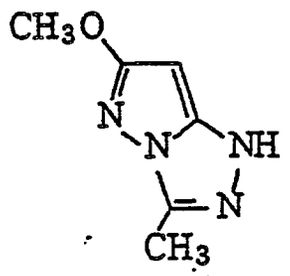

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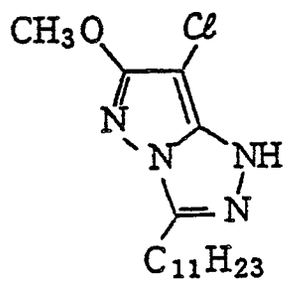

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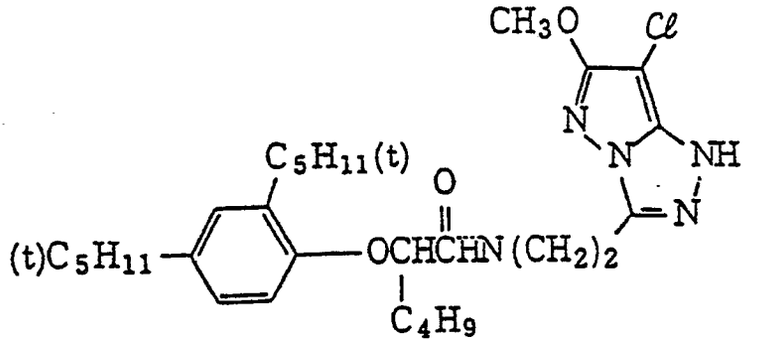

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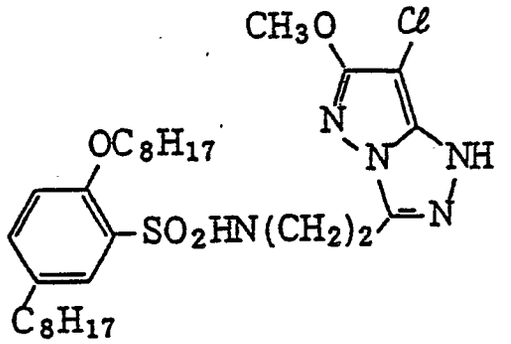

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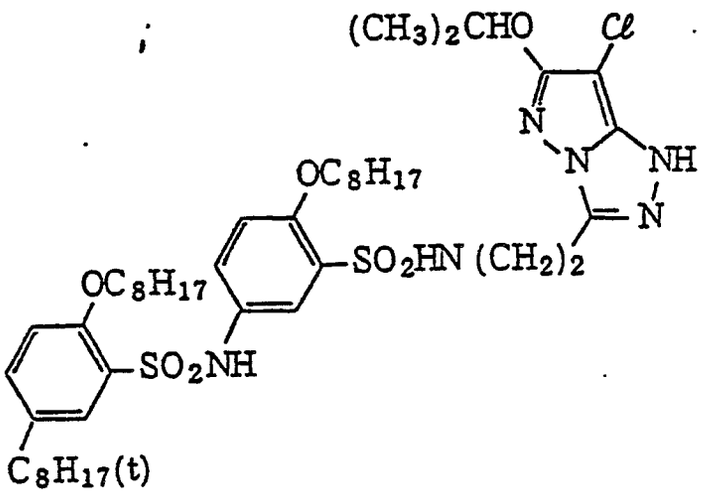

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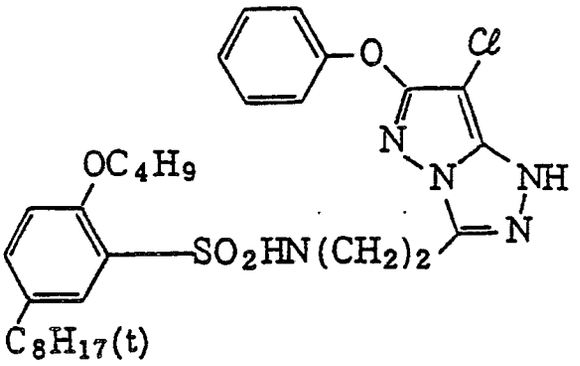

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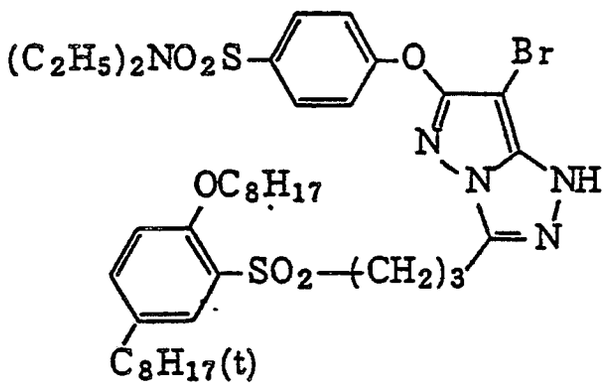

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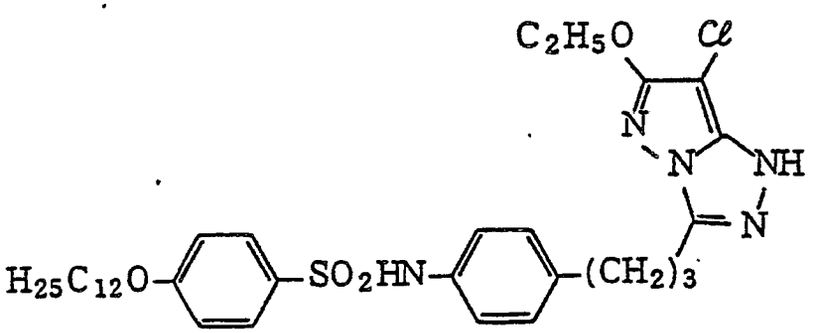

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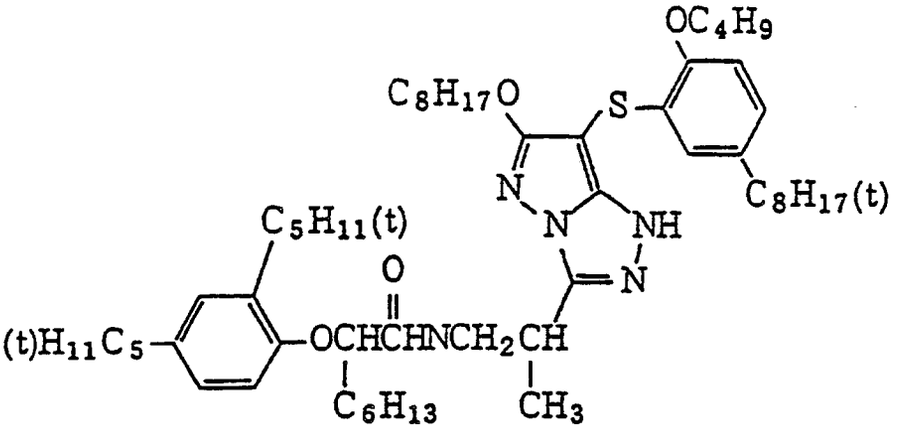

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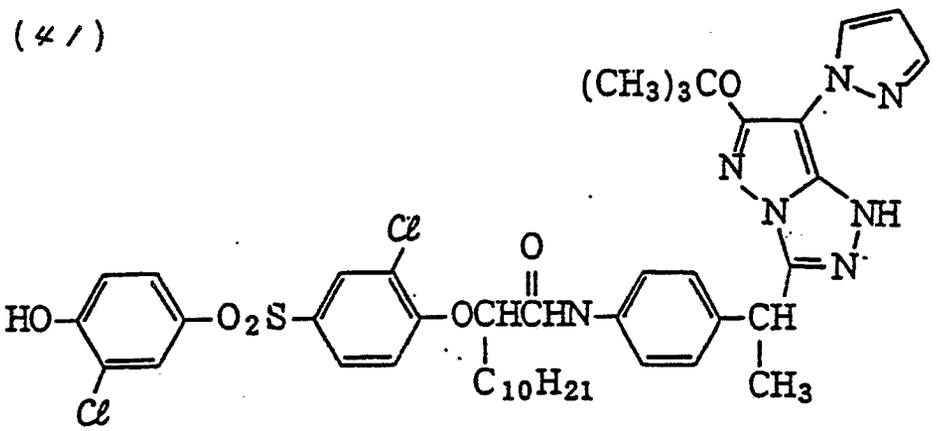

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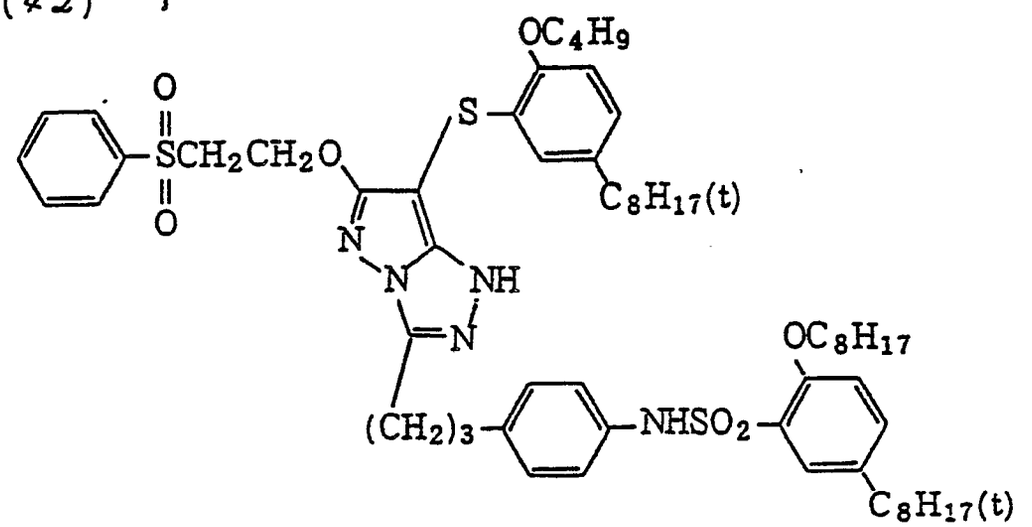

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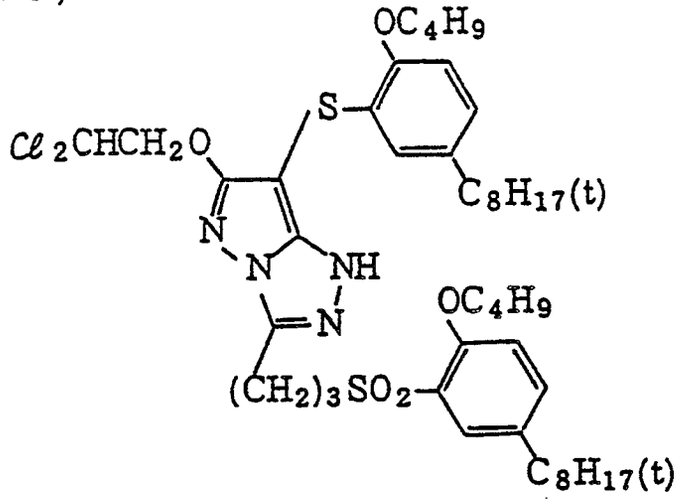

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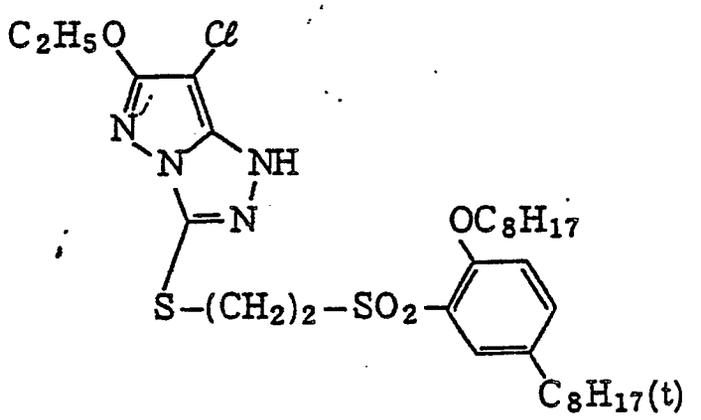

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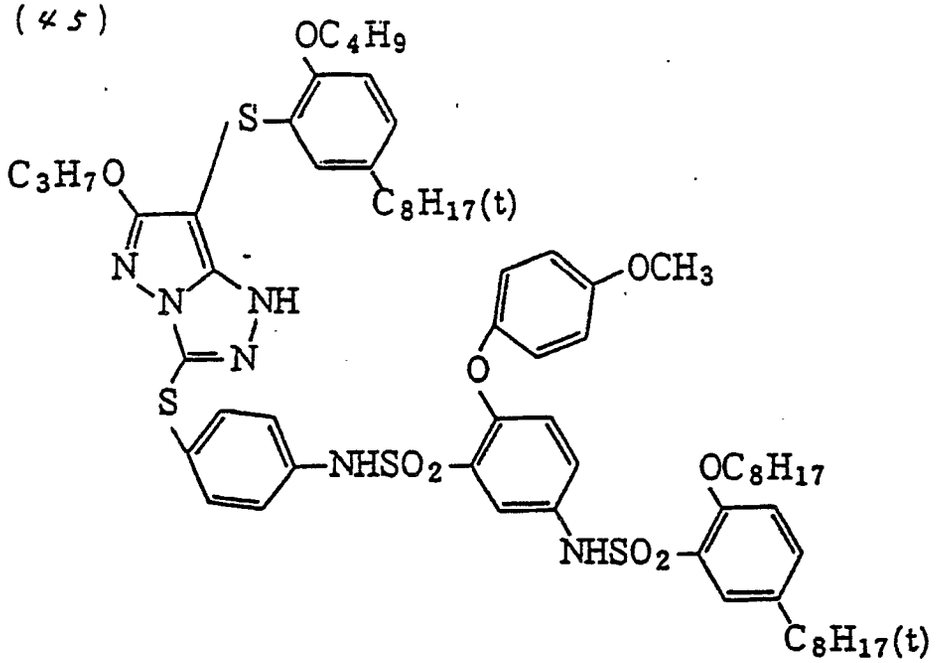

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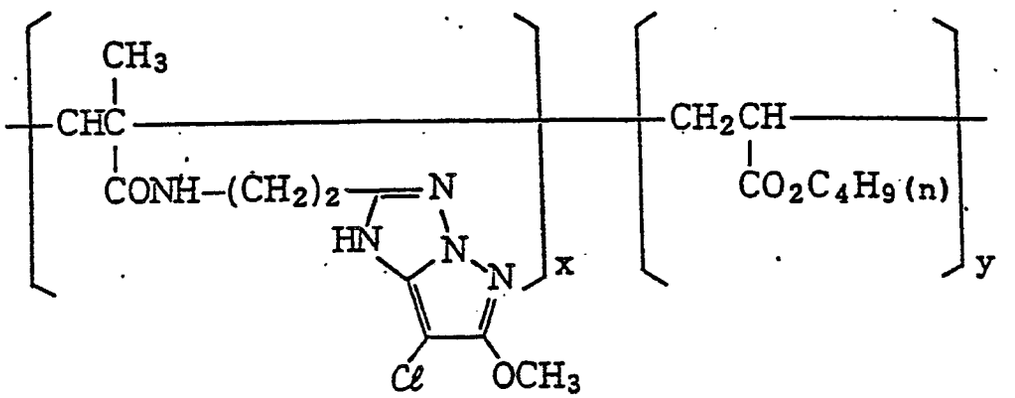
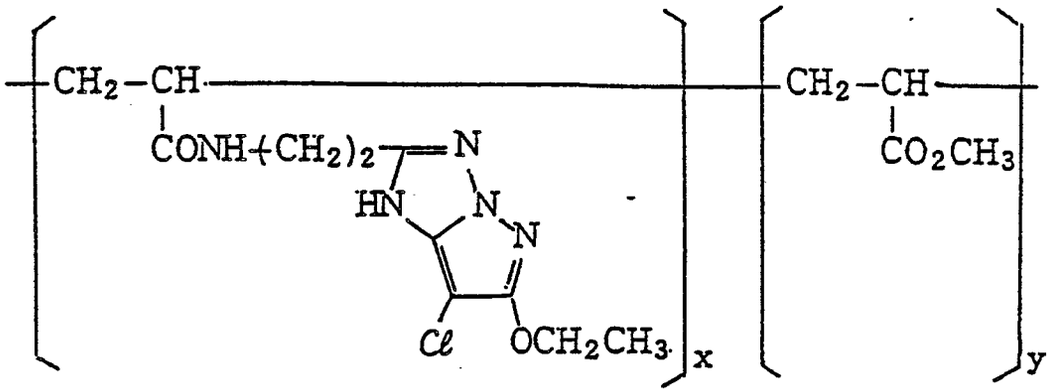


x : y = 50 : 50

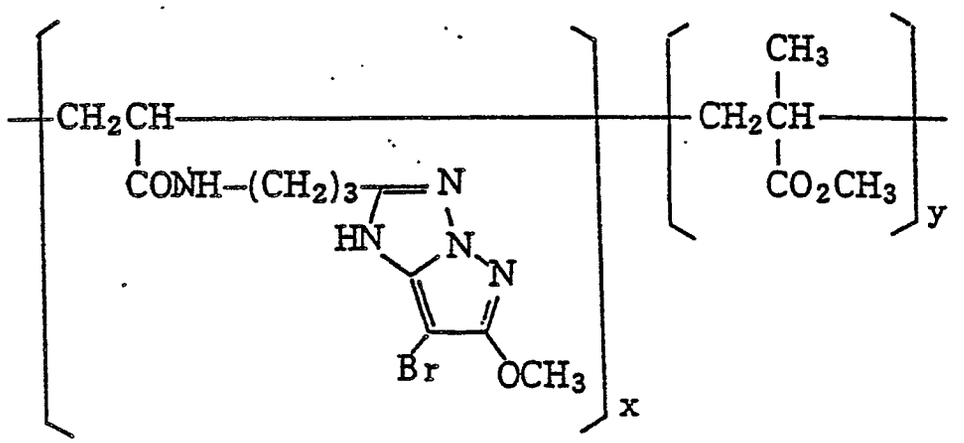
(by weight, hereinafter the the same)

(47)



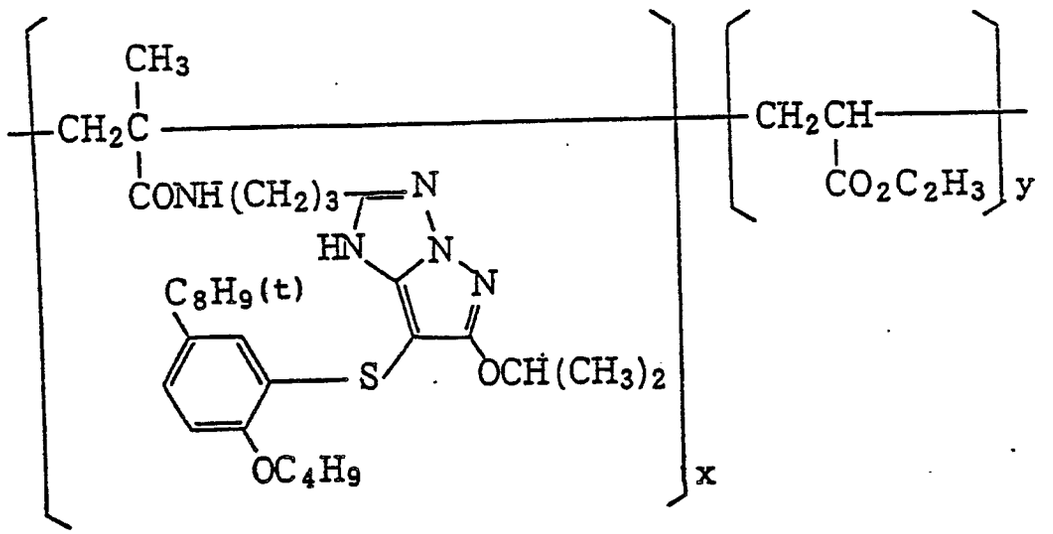
x : y = 45 : 55

(48)



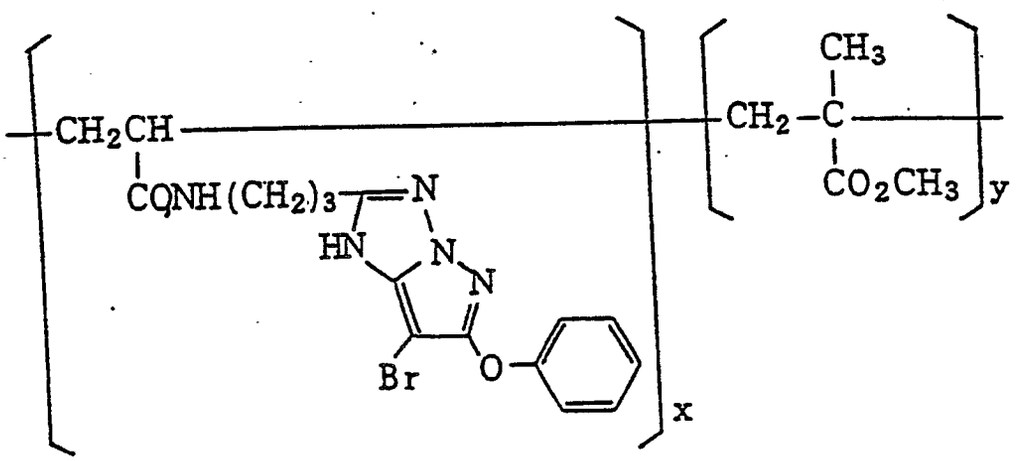
x : y = 45 : 55

(49)



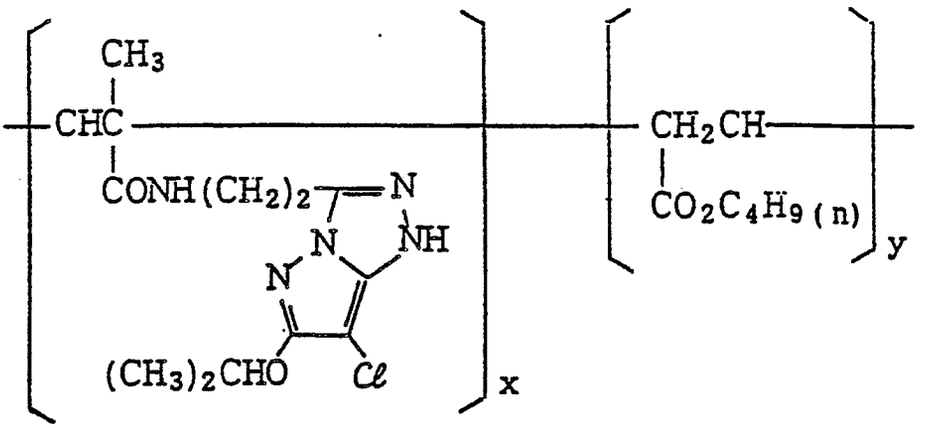
x : y = 50 : 50

(50)



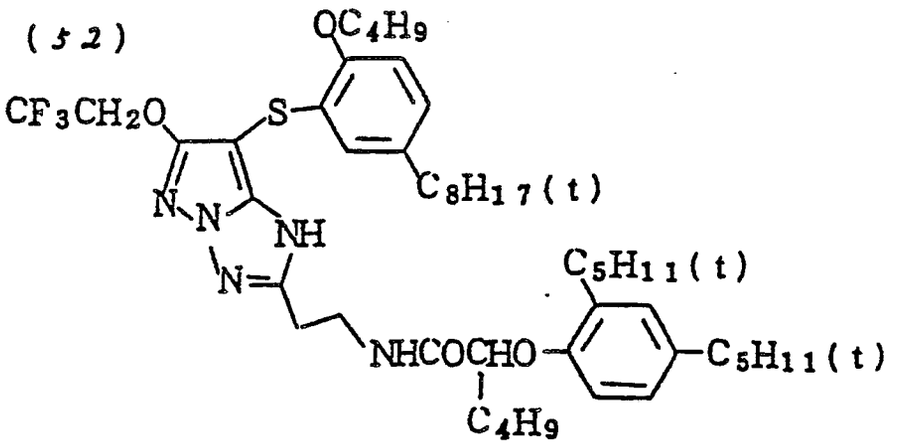
x : y = 45 : 55

(51)



x : y = 50 : 50

(52)



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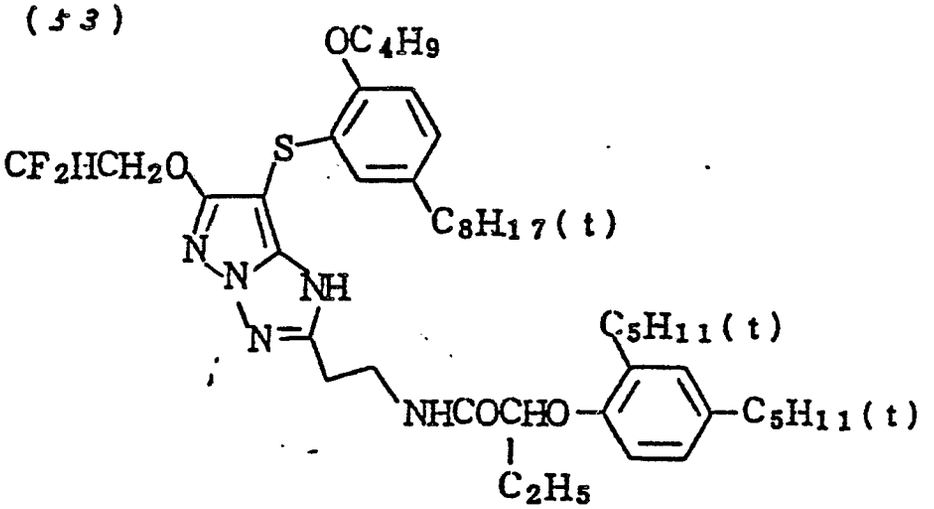

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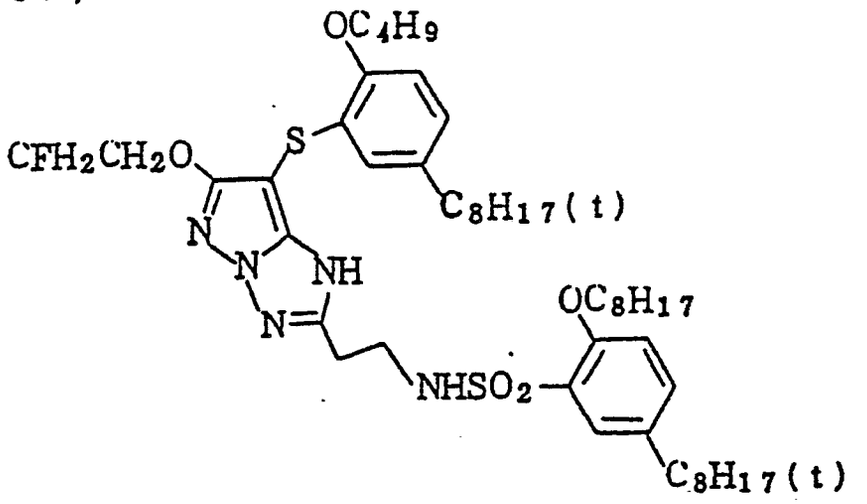
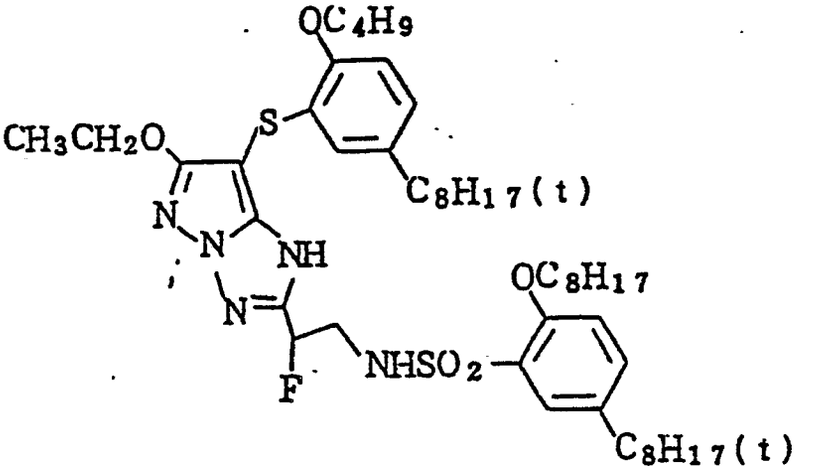
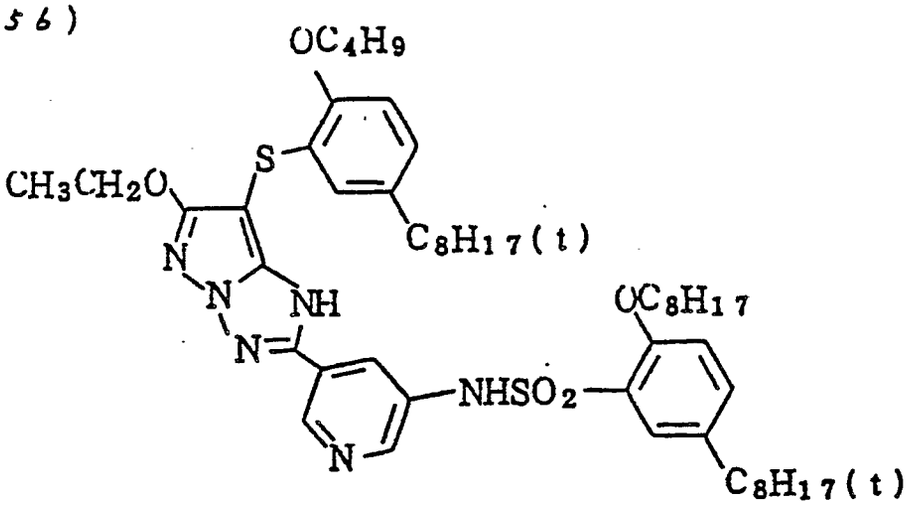

OC4H9
CFH2CH2O
S
C8H17(t)
N
N
NH
N
OC8H17
NHSO2
C8H17(t)

(55)


OC4H9
CH3CH2O
S
C8H17(t)
N
N
NH
N
OC8H17
F
NHSO2
C8H17(t)

(56)



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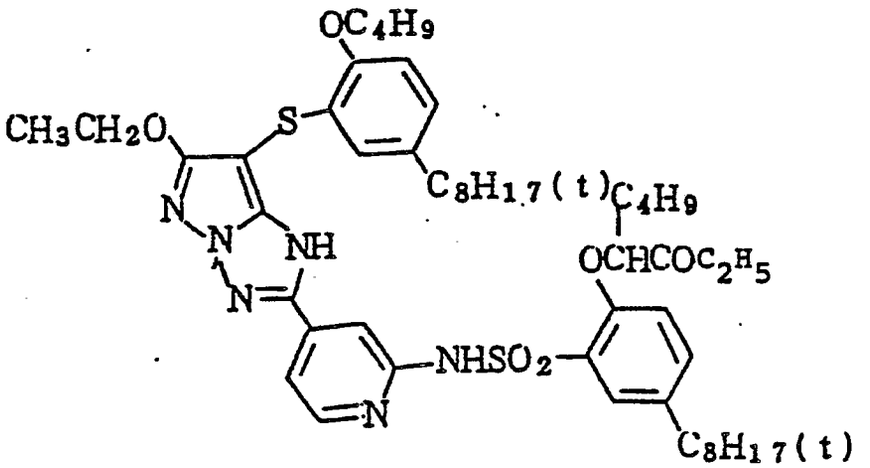

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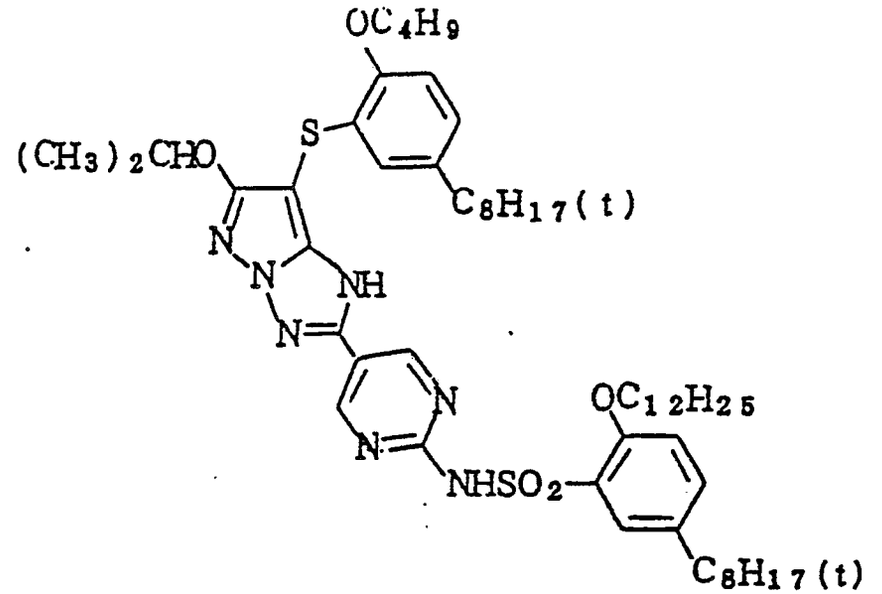

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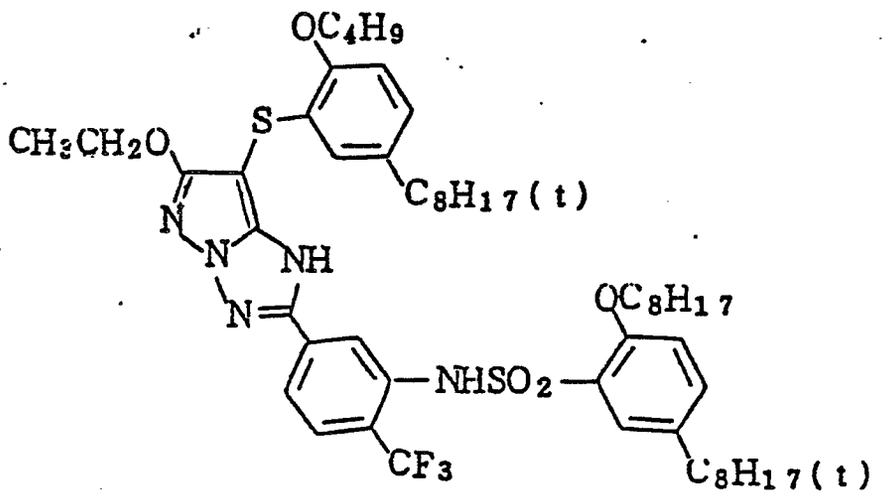

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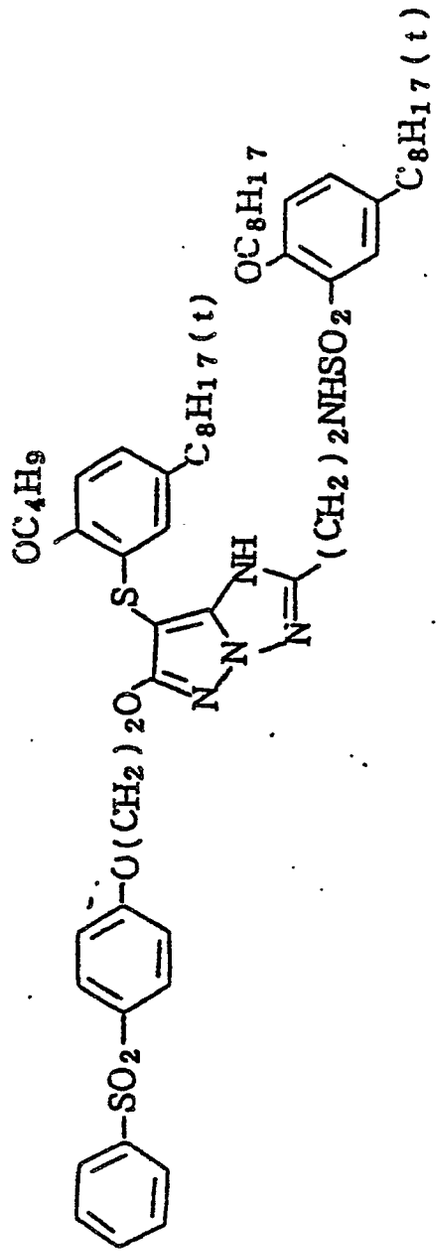

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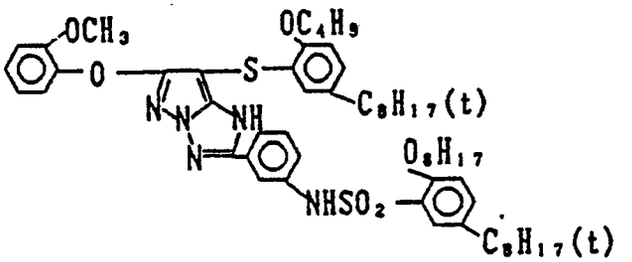

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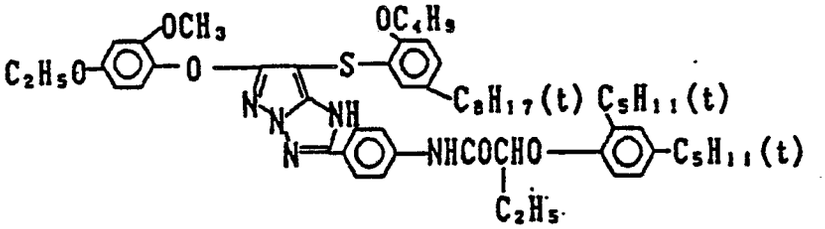

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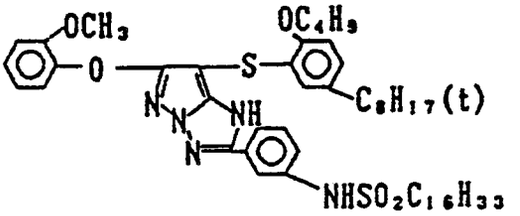

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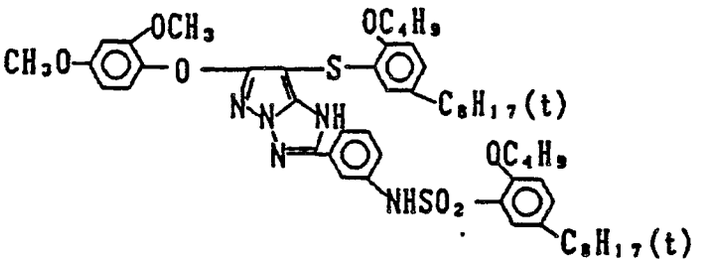

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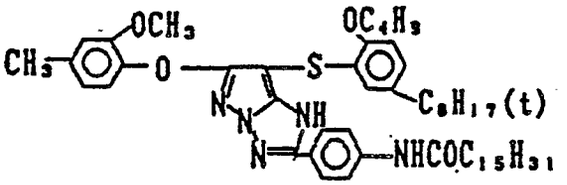

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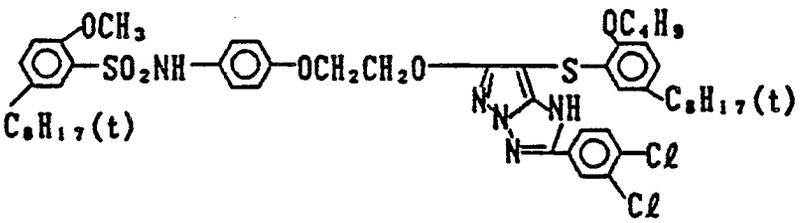

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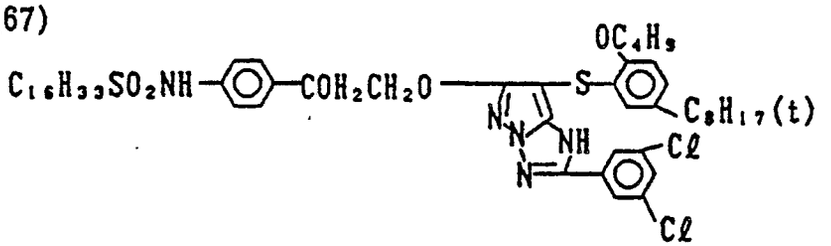

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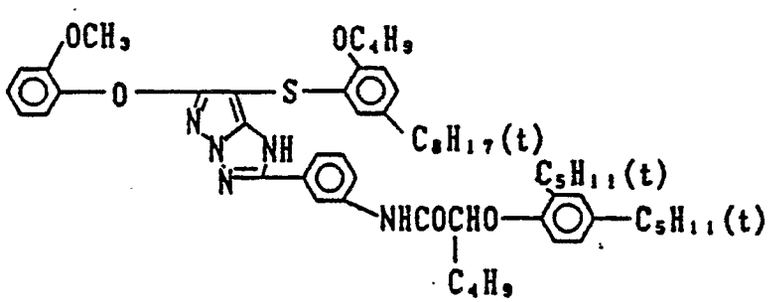

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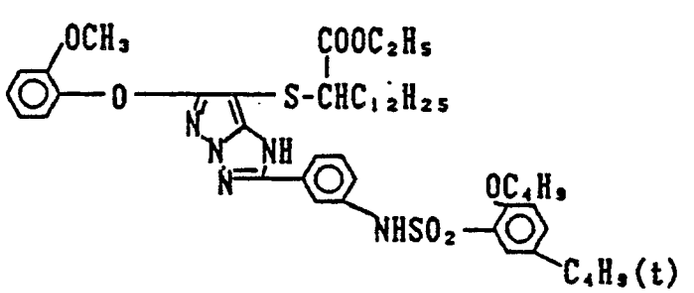

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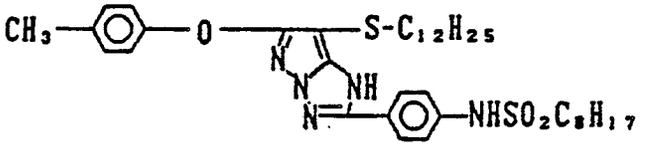

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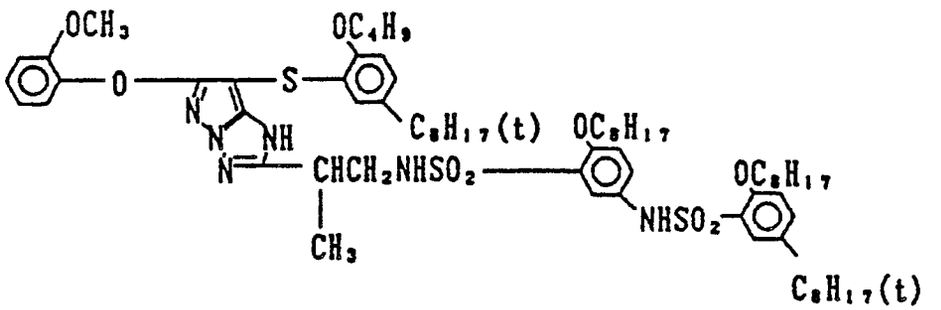

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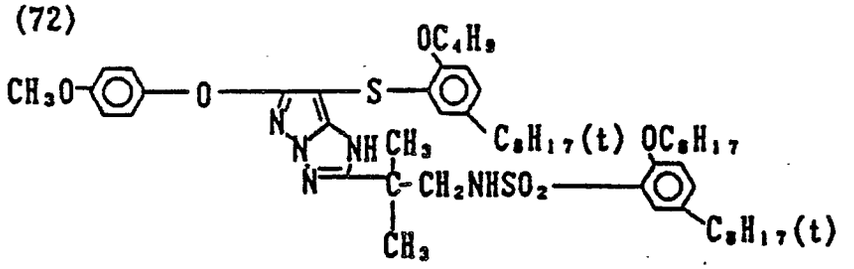

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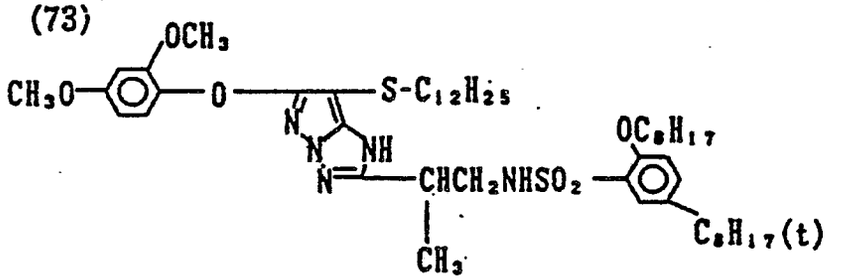

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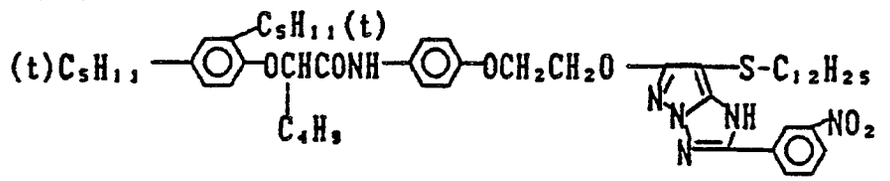

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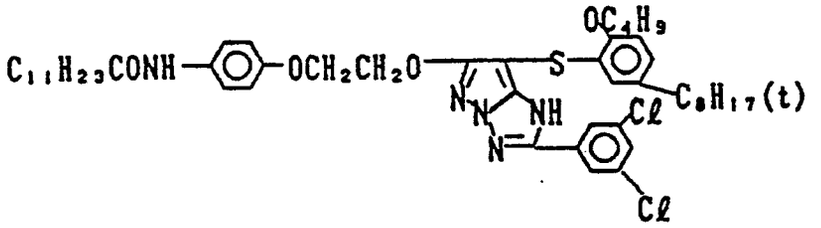

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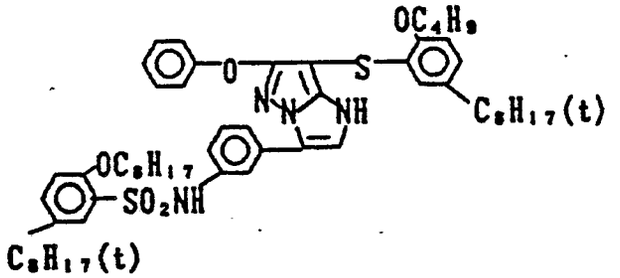

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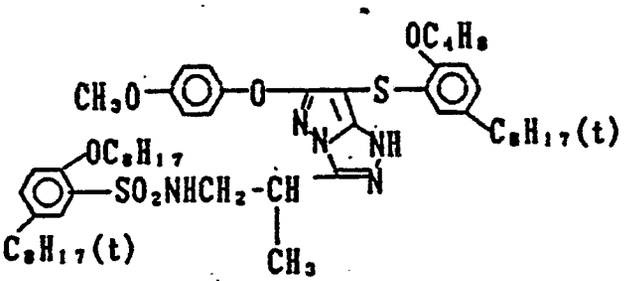

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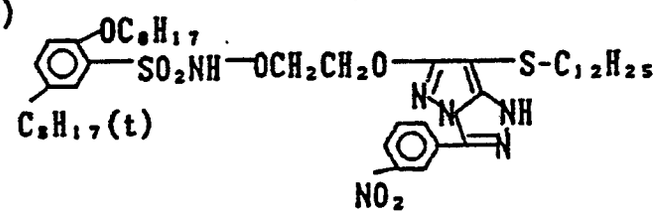

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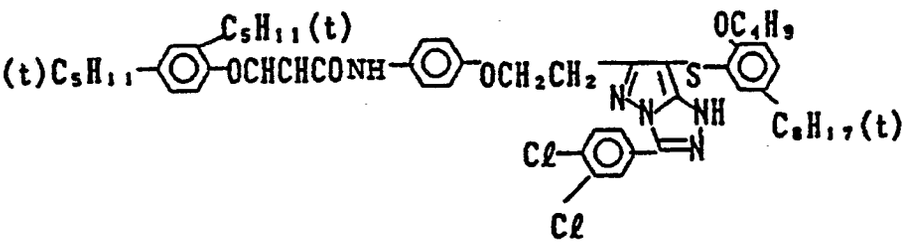

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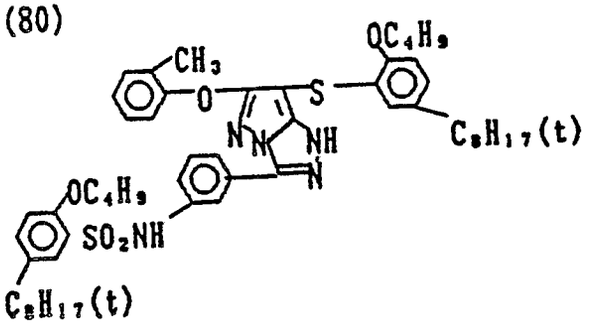

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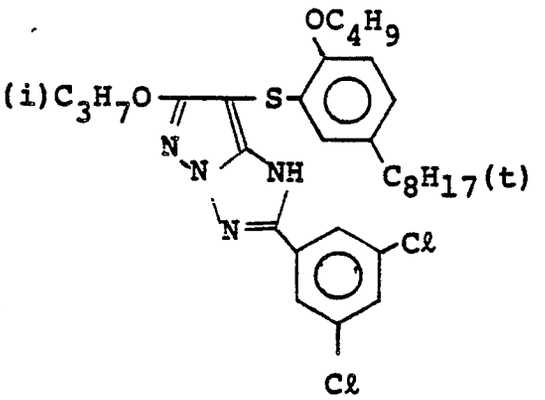

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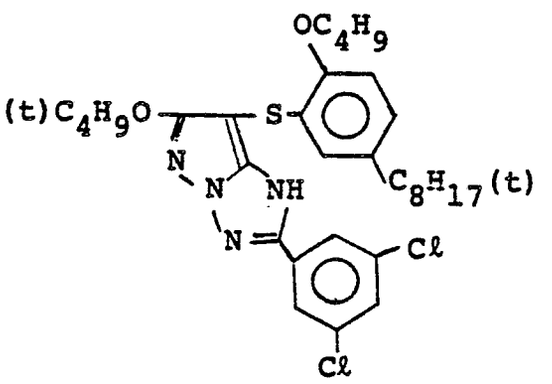


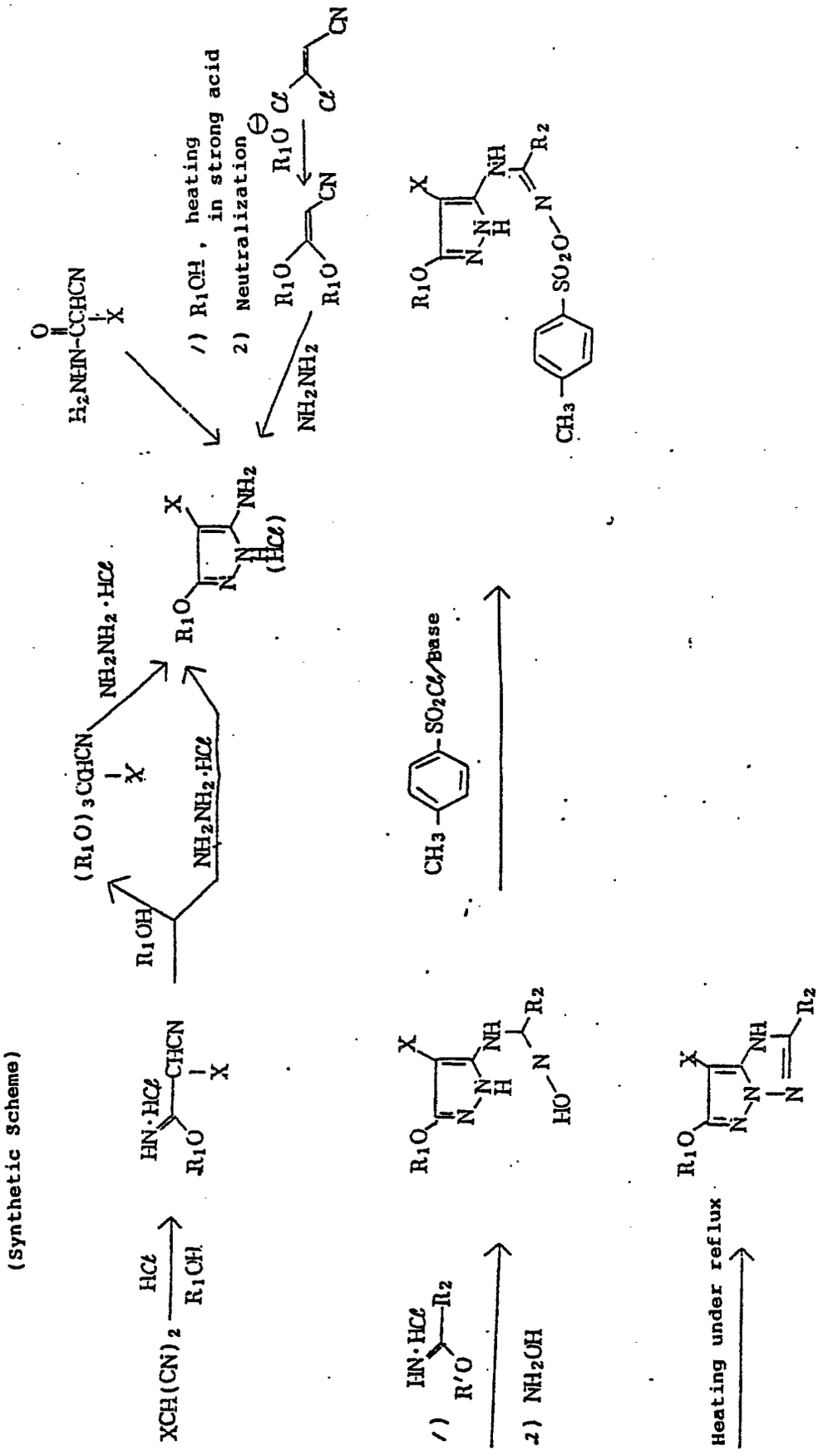
Of the couplers represented by the foregoing general formulae (I) and (II-A), those containing an aryl group, especially a substituted phenyl group (e.g., a phenyl substituted by an alkoxy group at the α-position), as R_1 are preferred over others.

General methods for synthesizing the couplers of the present invention are described below.

The synthesis methods for 1H-pyrazolo[1,5-b]-1,2,4-triazoles having a hydrogen atom and an alkyl group at their respective 6-positions are described in JP-A-60-197688. Basically, the couplers of the present invention (represented by the general formulae (I) and (II-A)), though differing in starting materials, can be synthesized by the same methods as cited above. The synthesis scheme is shown below. Details of other synthesis methods are described in Japanese Patent Application No. 62-175515, pp. 37 to 50.

The coupler represented by formula (I) or (II-A) is added in an amount of from 2×10^{-3} to 1 mol/Agmol, preferably from 1×10^{-2} to 5×10^{-1} mol/Agmol, to the light-sensitive silver halide layer.

(Synthetic Scheme)

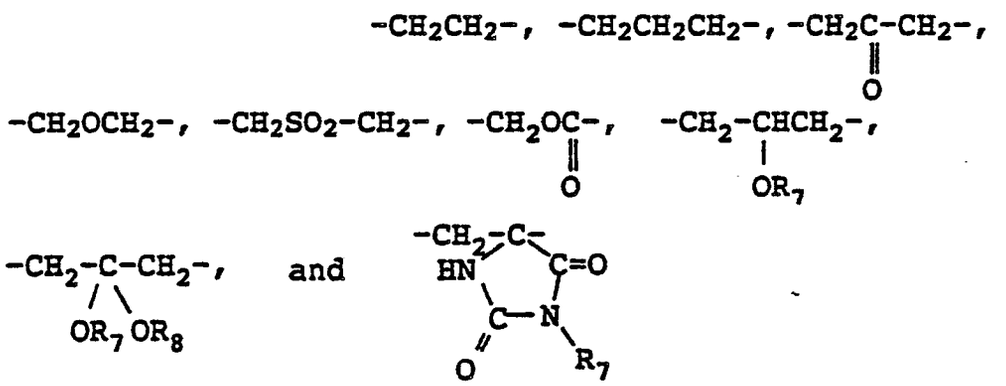


The compound represented by formula (III) is described in more detail below.

R represents hydrogen, an alkyl group (e.g., methyl, ethyl, butyl, isoamyl, octyl, hexadecyl), an alkenyl group (e.g., vinyl, allyl, 5-methyl-1-hexenyl, 1-octadecenyl), an alkynyl group (e.g., propynyl, 4-methyl-2-pentynyl, 5-tridecynyl, 1-octadecynyl), an oxy radical or hydroxyl. In particular, hydrogen is preferred as R.

R_3, R_4, R_5 and R_6 may be the same or different, and each represents hydrogen, or an alkyl group (e.g., methyl, ethyl, propyl, octyl, hexadecyl).

A represents a nonmetallic atomic necessary for forming a 5-, 6 or 7-membered ring, with specific examples including

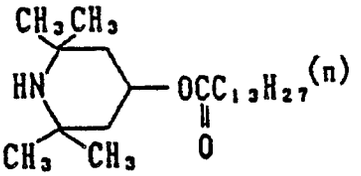


(wherein R_7 and R_8 may be the same or different, and each represents hydrogen, an alkyl group, an acyl group, a sulfonyl group, a sulfinyl group, or an alkoxycarbonyl group). Further, a 5- or 6-membered ring (e.g., cyclopentyl, cyclohexyl, cyclohexyl, pyran, piperazine, piperidine, morpholine) may be formed by combining R_3 with R_4, R_5 with R_6, R with R_3, or R_3 with A.

As for A, a nonmetallic atomic group forming a 5- or 6-membered ring, particularly those forming a piperidine ring, are preferred. As for R_3, R_4, R_5 and R_6, it is desirable that at least two of them, more preferably all of them, are an alkyl group. As for R, hydrogen or an alkyl group is preferred, and hydrogen is particularly preferred.

Specific examples of the compounds represented by the formula (III) are illustrated below. However, the invention is not to be construed as being limited to these examples.

Ⅲ－1



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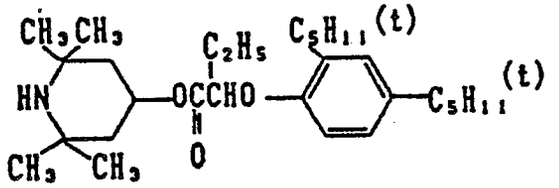

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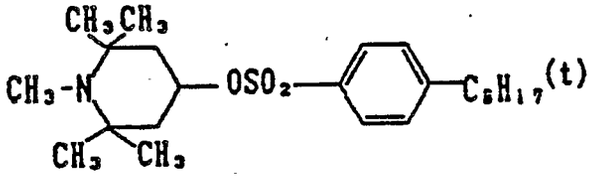

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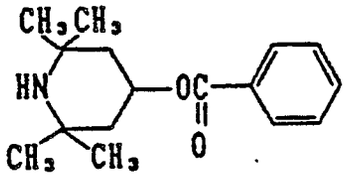

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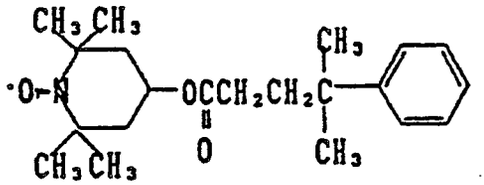

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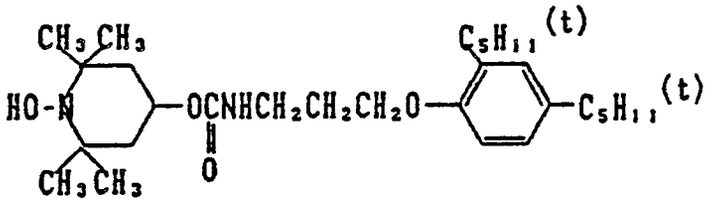

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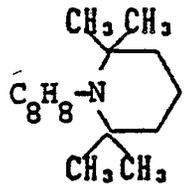

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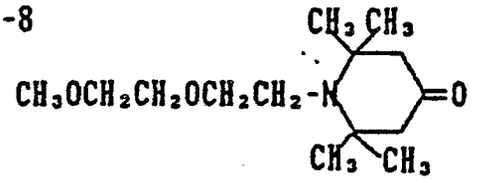

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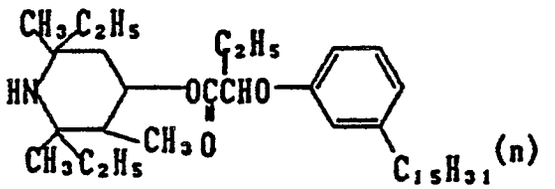

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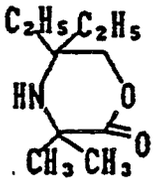

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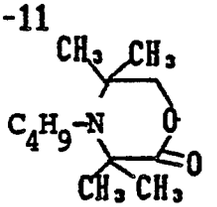

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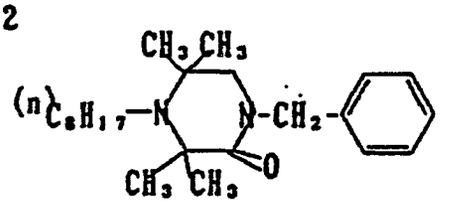

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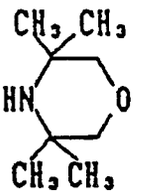

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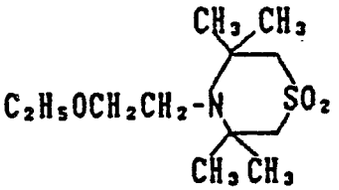

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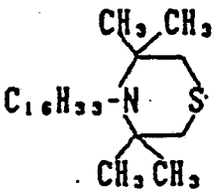

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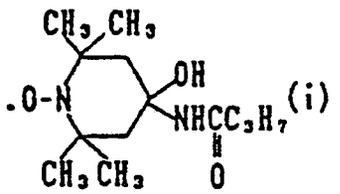

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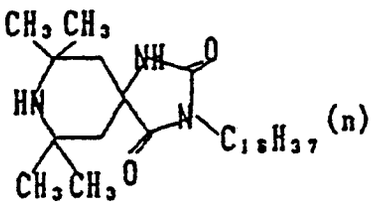

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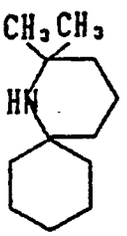

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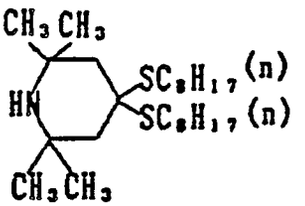

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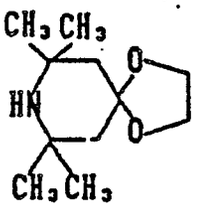

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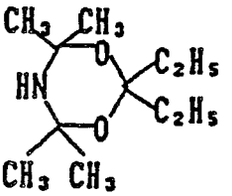

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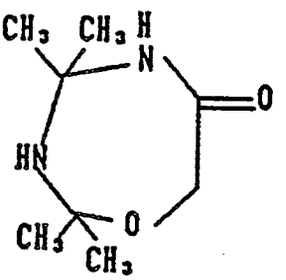

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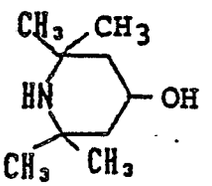

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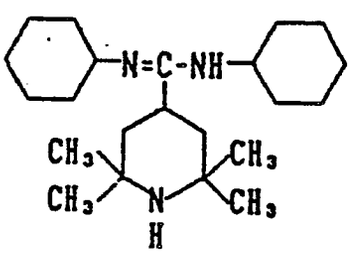

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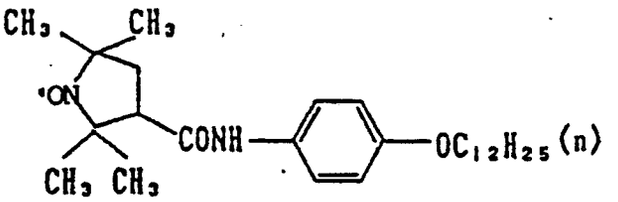

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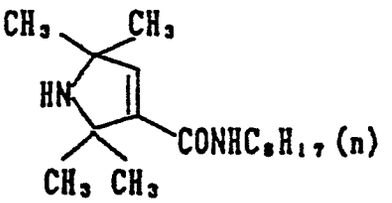

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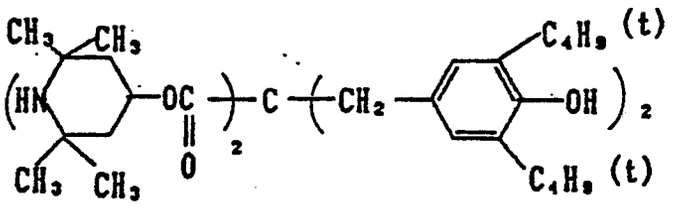

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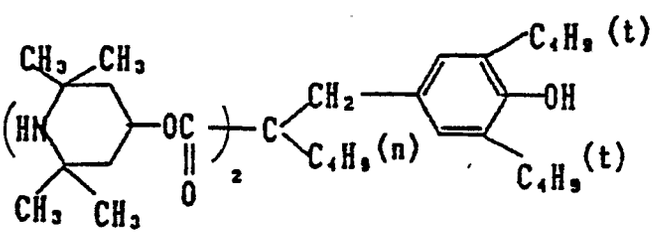

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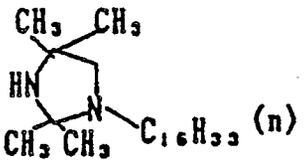

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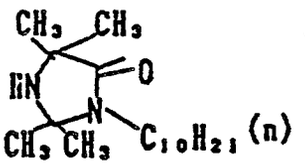

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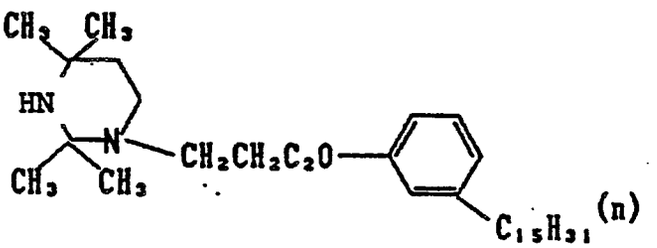

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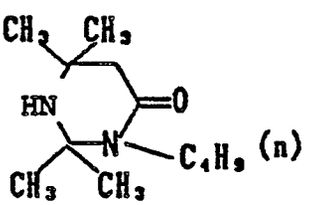

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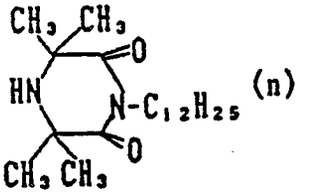

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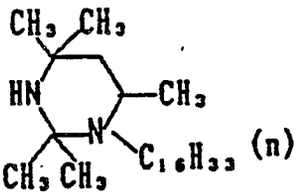

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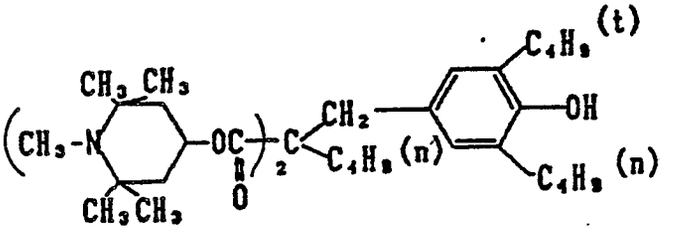

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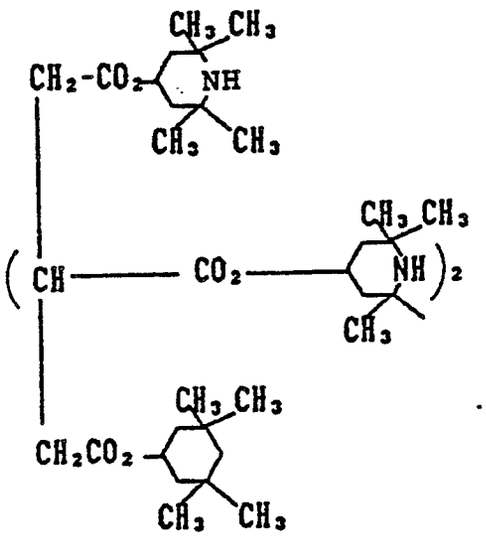

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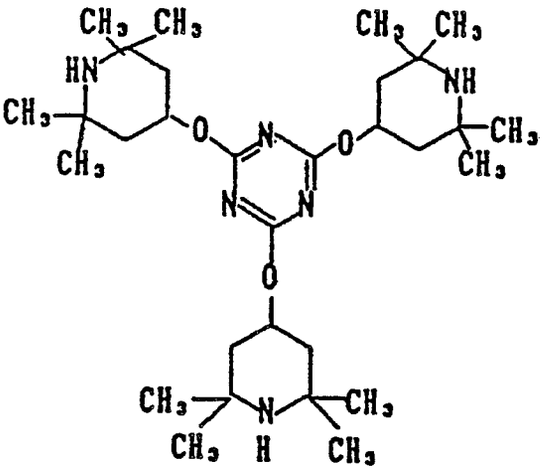
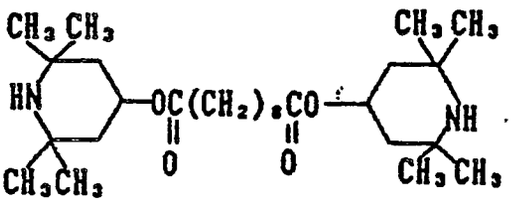
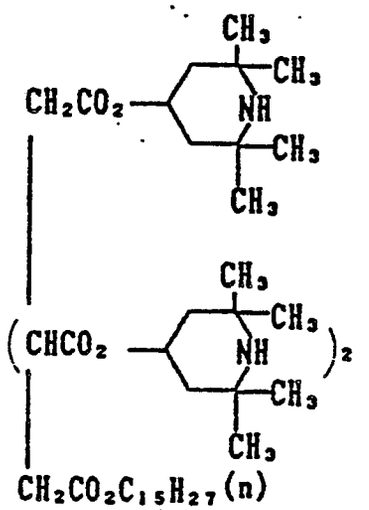


Ⅲ-38



Ⅲ-39



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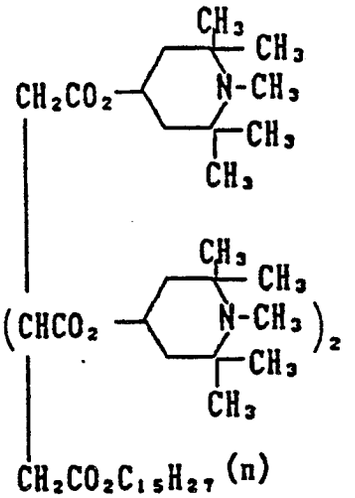

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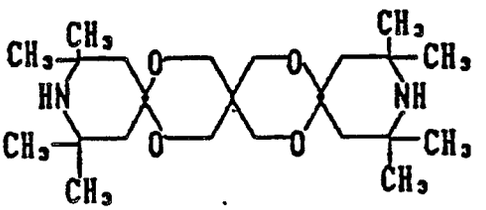

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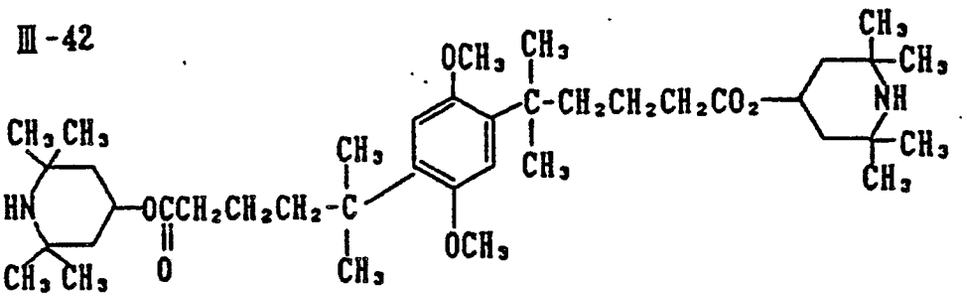

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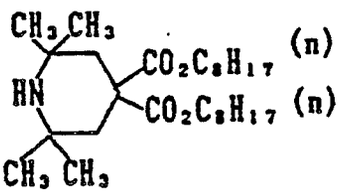

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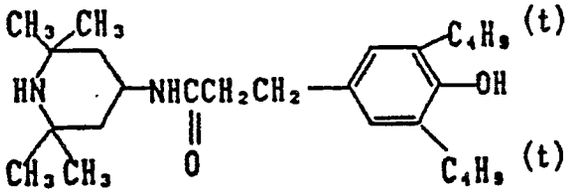

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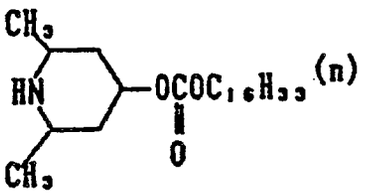
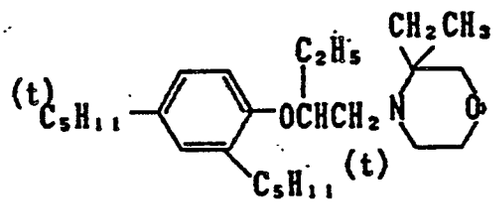
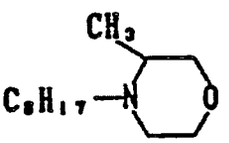


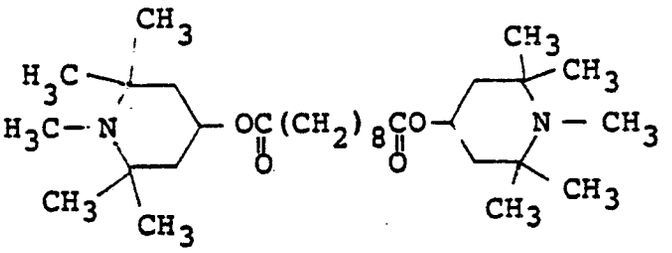
Ⅲ-46



Ⅲ-47



(III-48)



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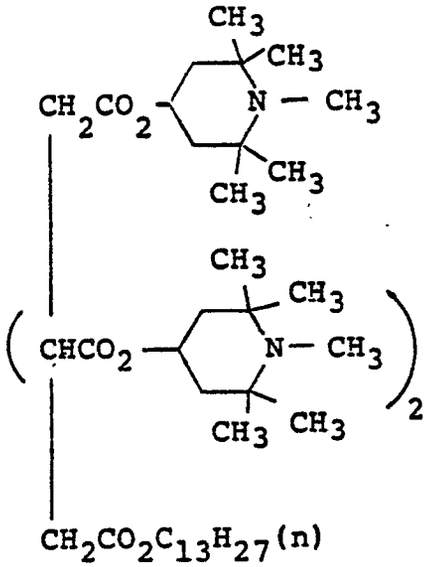

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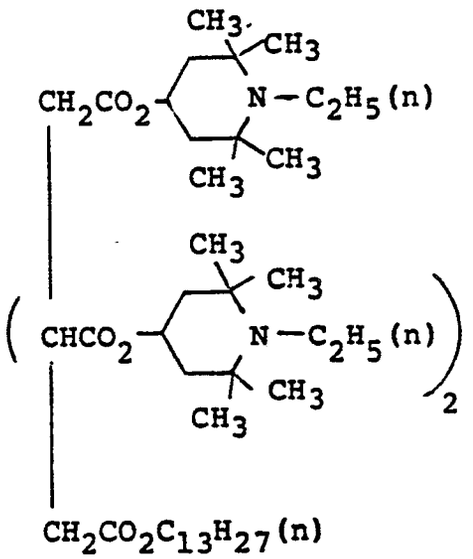
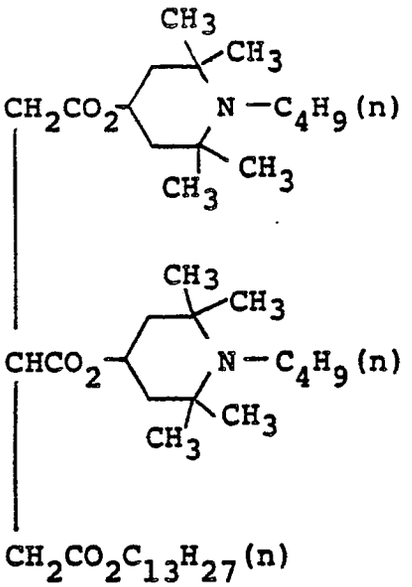
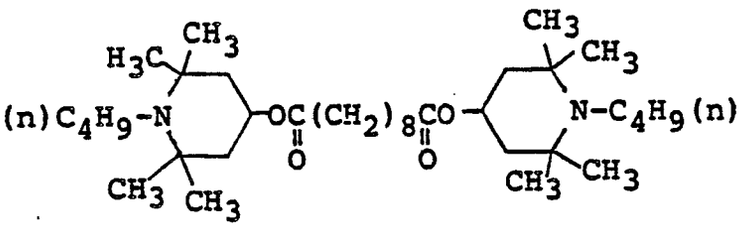


(III-51)



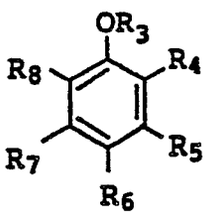
(III-52)



These compounds can be synthesized in accordance with the methods described in JP-A-49-53572, JP-A-49-53573, JP-A-49-53574, JP-A-49-53575, JP-A-49-7180, JP-B-51-1420 (the term "JP-B" as used herein means an "examined Japanese patent publication"), British Patents 1,326,889, 1,354,313 and 1,410,846, and U.S. Patents 4,268,593 and 4,452,884.

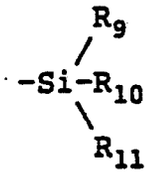
These compounds are added in a proportion of 5 to 200 mol%, preferably 10 to 50 mol%, to the coupler.

Image stabilizers which are preferably used together with the compounds of the present invention, include compounds represented by the general formula (IV), and metal complexes.



(IV)

In the foregoing formula, R_3 represents hydrogen, an alkyl group, an alkenyl group, an aryl group, a heterocyclic group, or



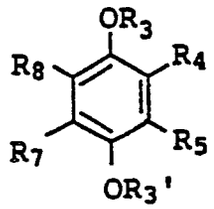
(wherein R_9, R_{10} and R_{11} may be the same or different, and each represents an alkyl group, an alkenyl group, an aryl group, an alkoxy group, an alkenoxy group or an aryloxy group). R_4, R_5, R_6, R_7 and R_8 may be the same or different, and each represents hydrogen, an alkyl group, an alkenyl group, an aryl group, an acylamino group, an alkylamino group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, an aryloxycarbonyl group, a halogen atom or $-O-R_3'$, wherein R_3' has the same meaning as R_3. R_3 and R_4 may combine with each other to form a 5-membered ring, a 6-membered ring or a spiro ring. Also, R_4 and R_5, or R_5 and R_6 may combine with each other to form a 5-membered ring, a 6-membered ring or a spiro ring.

More detailed descriptions of R_4, R_5, R_6, R_7 and R_8 are given below.

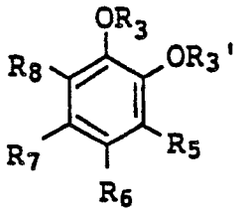
R_4, R_5, R_6, R_7 and R_8 may be the same or different, and each represents hydrogen, an alkyl group (e.g., methyl, n-butyl, n-octyl, sec-dodecyl, t-butyl, t-amyl, t-hexyl, t-octyl, t-octadecyl, α,α-dimethylbenzyl, 1,1,-dimethyl-4-hexyloxycarbonylbutyl), an alkenyl group (e.g., vinyl, allyl), an aryl group (e.g., phenyl, naphthyl, p-methoxyphenyl, 2,4-t-butylphenyl), an acylamino group (e.g., acetylamino, propionylamino, benzamino), an alkylamino group (e.g., N-methylamino, N,N-dimethylamino, N,N-dihexylamino, piperidino, N-cyclohexylamino, N-(t-butyl)amino), an alkylthio group (e.g., methylthio, n-butylthio, sec-butylthio, t-butylthio, dodecylthio), an arylthio group (e.g., phenylthio, naphthylthio), an alkoxycarbonyl group (e.g., methoxycarbonyl, n-octyloxycarbonyl), an aryloxycarbonyl group (e.g., phenyloxycarbonyl, naphthyloxycarbonyl, 4-methoxy-2-t-butylphenoxycarbonyl, 2,4-di-t-butylphenyloxycarbonyl), a halogen atom (e.g., chlorine, bromine), or $-O-R_3'$, wherein R_3' represents the same group as R_3. R_3 may combine with R_4 or R_5 to form a 5-membered, 6-membered or spiro ring. Specific examples of a ring formed by combining R_3 with R_4 include a chroman ring, a coumarane ring, and methylenedioxybenzene. Also, R_4 and R_5, or R_5 and R_6 may combine with each other to form a 5-membered, 6-membered or spiro ring, including an indane ring and a spiroindane ring.

Of the compounds represented by the general formula (IV), those represented by the following general formulae (IV-1) to (IV-5) are preferred.

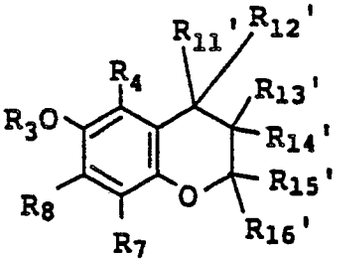
(IV-1)



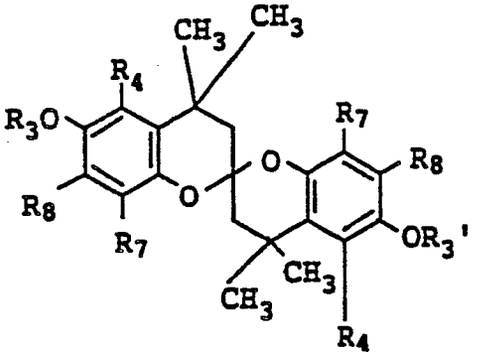
(IV-2)



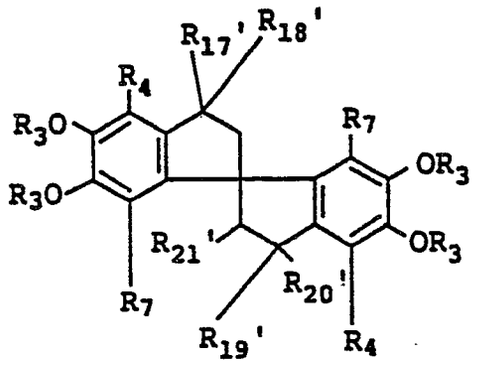
(IV-3)



(IV-4)



(IV-5)

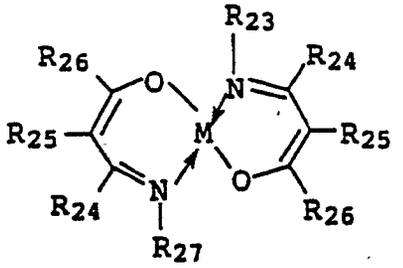


In the general formulae (IV-1) to (IV-5), R_3, R_3', R_4, R_5, R_6, R_7 and R_8 have the same meanings as those in formula (IV), respectively. R_{11}' through R_{21}' may be the same or different, and each represents hydrogen, an alkyl group or an aryl group.

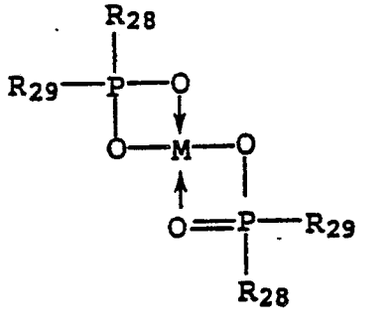
Of the compounds represented by the general formulae (IV-1) to (IV-5), those having alkyl groups or aryl groups, especially alkyl groups, as R_3 and R_3', are preferred. Further, it is desirable that R_4 to R_8 should be those selected from hydrogen, alkyl groups and aryl groups.

Also, it is preferred that the compound of the present invention should be used together with metal complexes. Metal complexes which can be used in the present invention are compounds containing copper, cobalt, nickel, palladium or platinum as the central metal, and at least one bidentate or higher organic ligand. As for the central metal, nickel is particularly preferred. As for the coordination atoms which are coordinately bonded to the central metal, nitrogen, sulfur, oxygen and phosphorus are preferred.

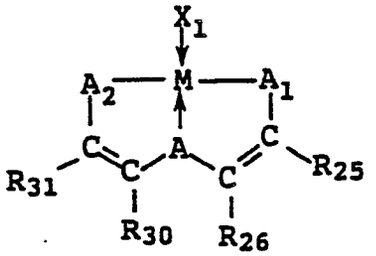
Structures of metal complexes which are particularly preferred in the present invention are represented by the following general formulae (V-1) to (V-4).



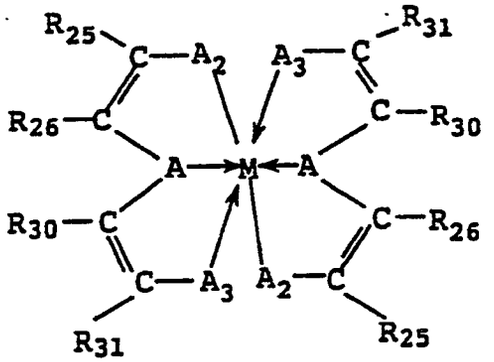
(V-1)



(V-2)



(V-3)



(V-4)

In the foregoing general formulae (V-1) to (V-4), M represents Cu, Co, Ni, Pd, or Pt. R_{23} and R_{27} may be the same or different, and each represents hydrogen, an alkyl group, an aryl group, or a hydroxyl group. Further, R_{23} and R_{27} be linked, R_{24} represents hydrogen, an alkyl group, or an aryl group. R_{25} and R_{26} may be the same or different, and each represents hydrogen, an alkyl group, or an aryl group. Further, R_{25} and R_{26} may be linked to form an aromatic ring or a 5- to 8-membered ring. R_{30} and R_{31} have the same meanings as R_{25} and R_{26}. R_{28} and R_{29}, which may be the same or different, each represents an alkyl group, an aryl group, an alkylthio group, an arylthio group, an alkoxy group, an aryloxy group, an alkylamino group, or an arylamino group. Of the substituent groups present in the general formulae (V-1) to (V-4), those having an alkyl moiety or an aryl moiety may be further substituted by a substituent group.

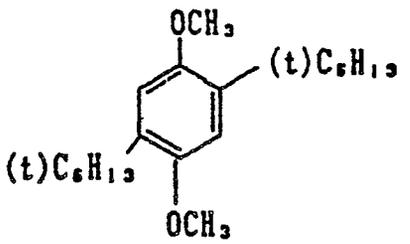
X_1 represents a compound capable of coordinately bonding to M. Specific examples of such compound include H_2O and organic or inorganic amines (e.g., pyridine, triethylamine, ammonia). A represents oxygen, sulfur or $-NR_{110}-$, wherein R_{110} represents hydrogen, an alkyl group, an aryl group, a hydroxyl group, or an alkoxy group. A_1 and A_2, which may be the same or different, each represents oxygen, sulfur, or an amine group. A_3 represents a hydroxyl group, an alkoxy group, an alkylthio group, or $-NR_{120}R_{130}$, wherein R_{120} and R_{130} may be the same or different, and each represents hydrogen or an alkyl group.

Of the metal complexes represented by formulae (V-1) to (V-4), those represented by formula (V-1) are

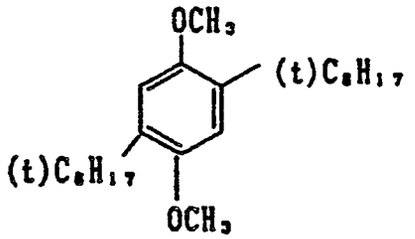
preferred.

Specific examples of the compounds represented by formula (IV), and those of the metal complexes are illustrated below. However, the invention is not to be construed as being limited to these examples.

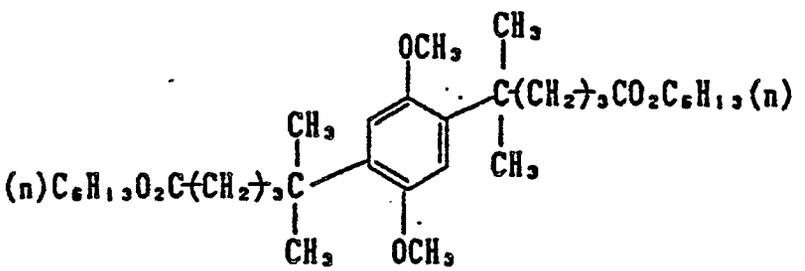
A-1



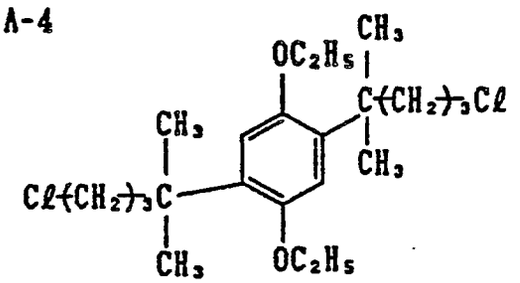
A-2



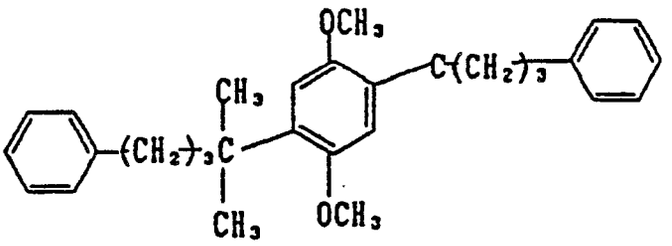
A-3



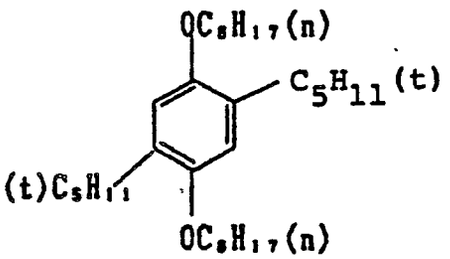
A-4



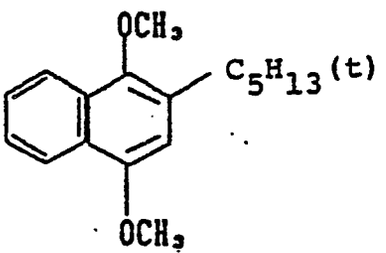
A-5



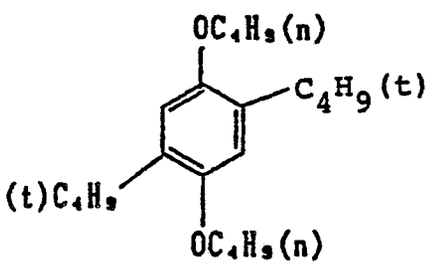
A-6



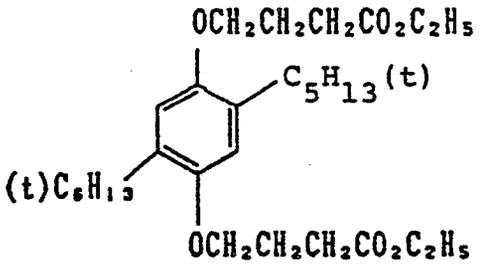
A-7



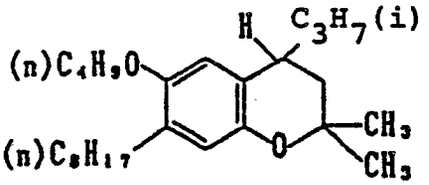
A-8



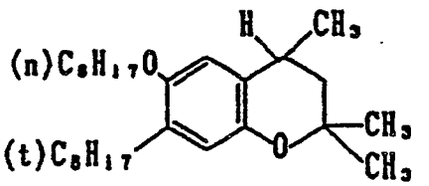
A-9



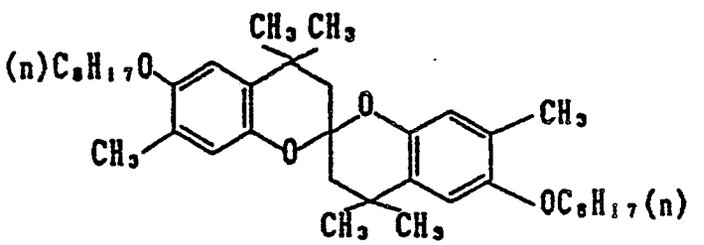
A-10



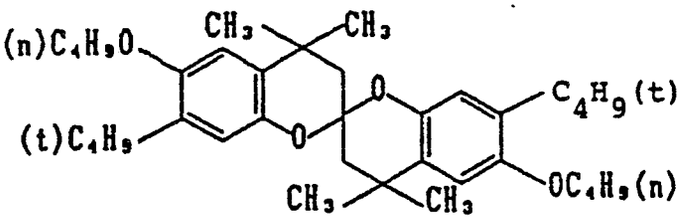
A-11



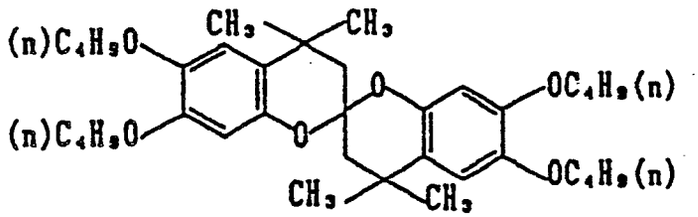
A-12



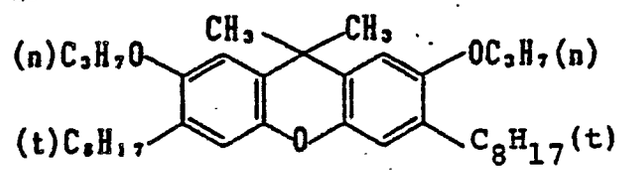
A-13



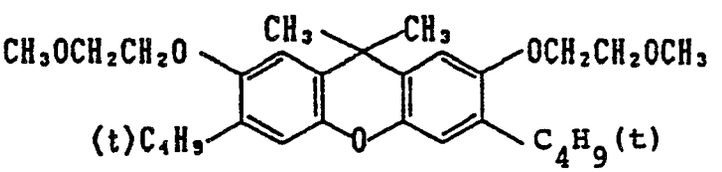
A-14



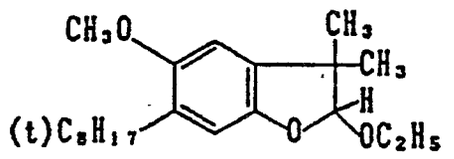
A-15



A-16



A-17



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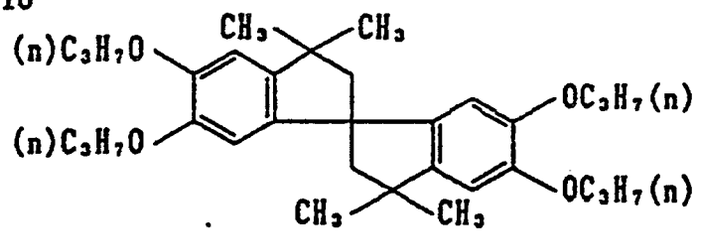

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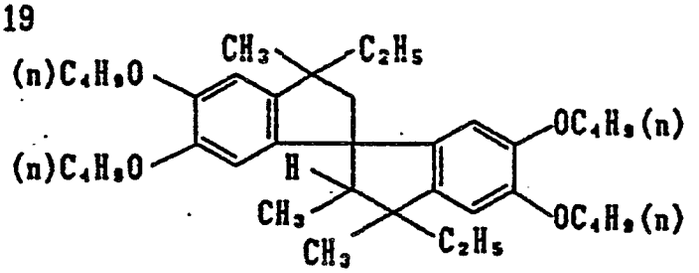

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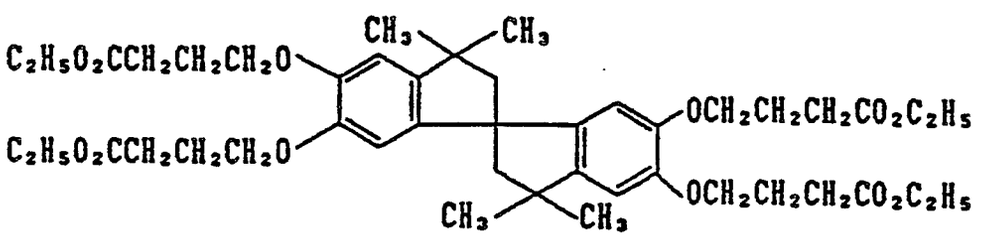

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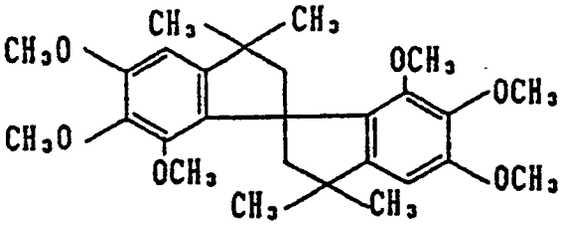

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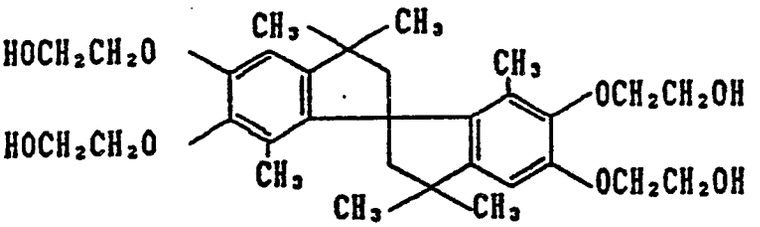

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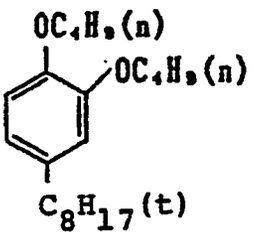

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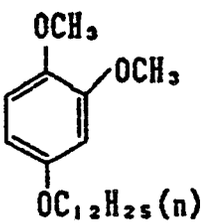

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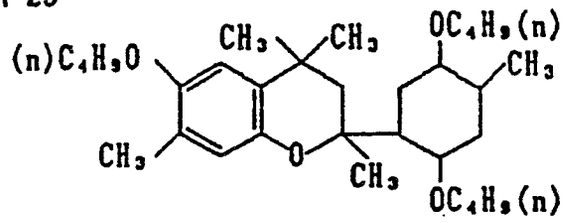

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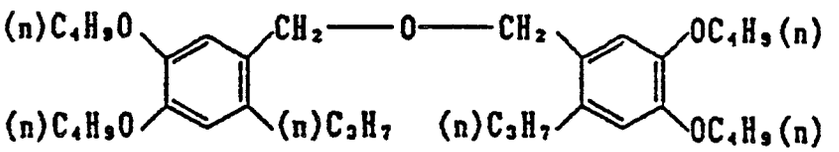

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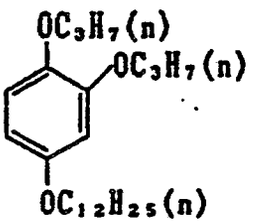

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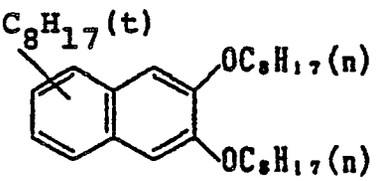

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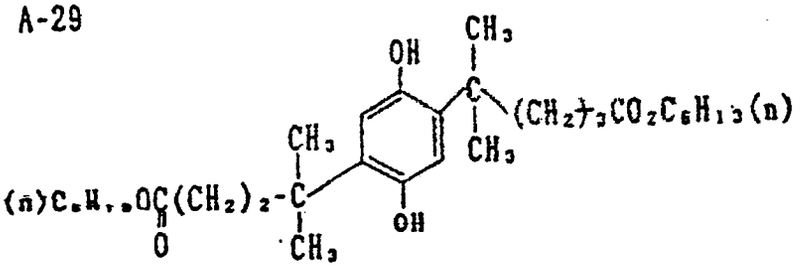

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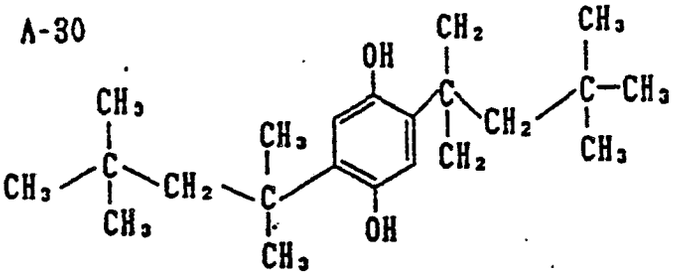

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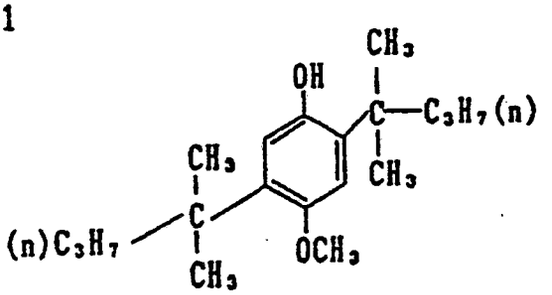

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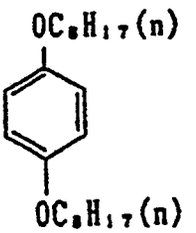

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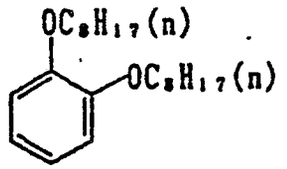

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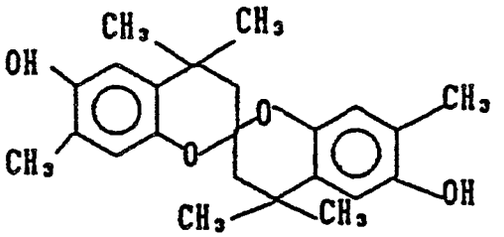

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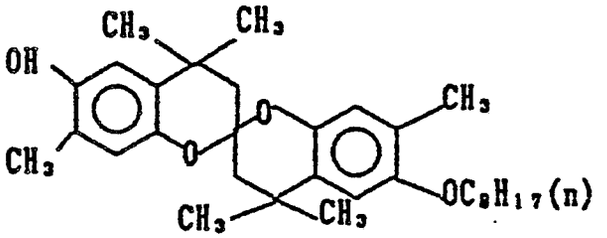

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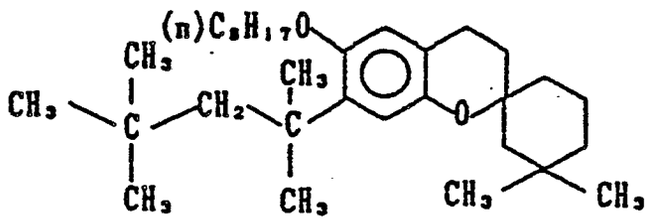

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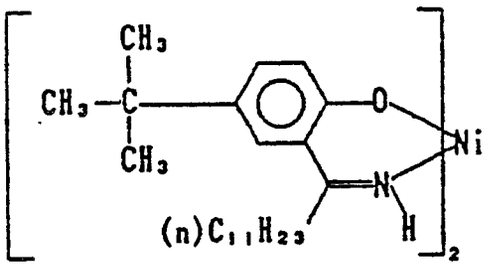

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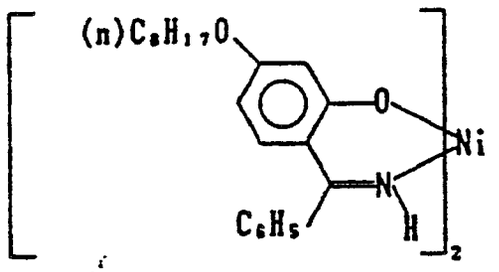

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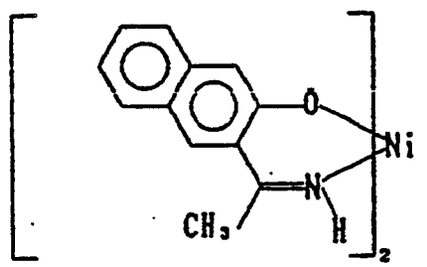

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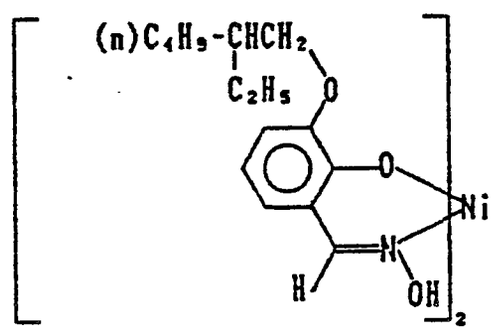

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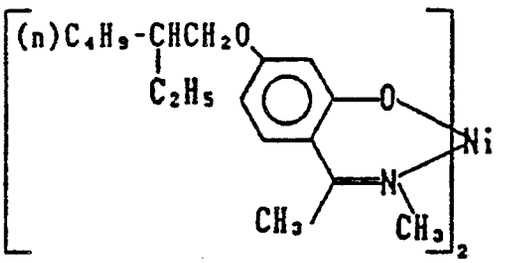

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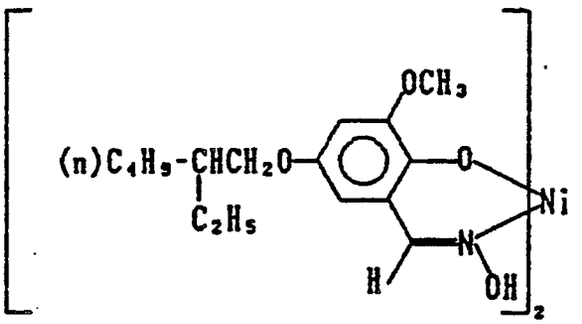

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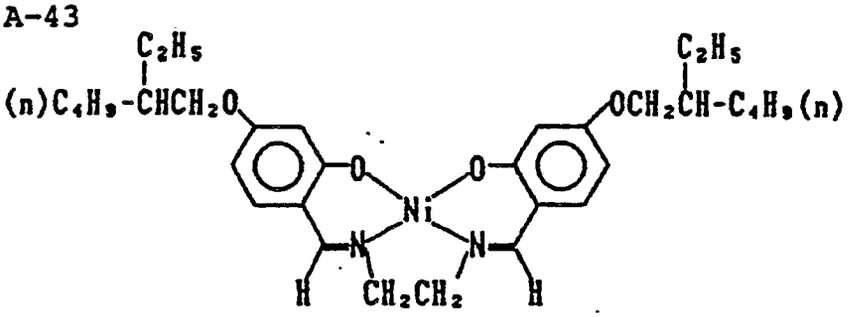

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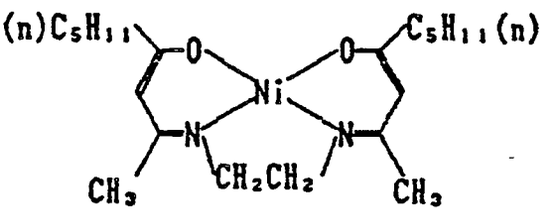

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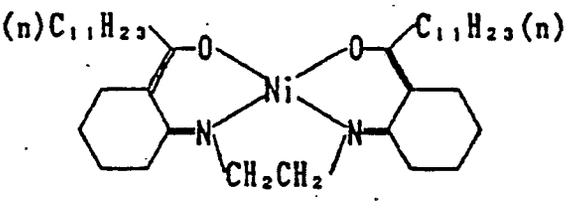

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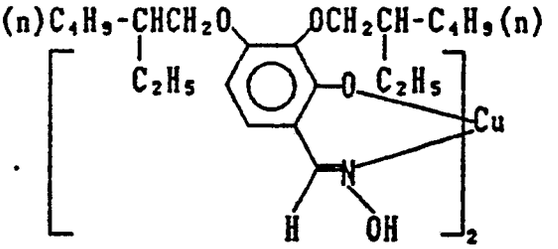

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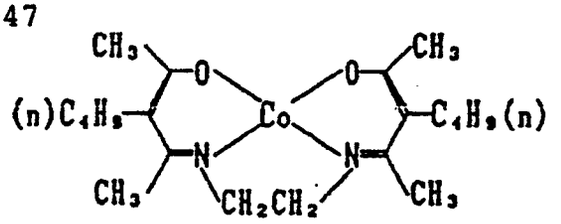

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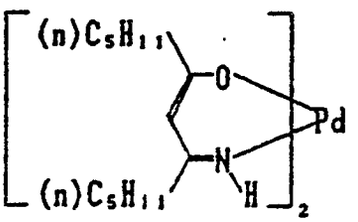

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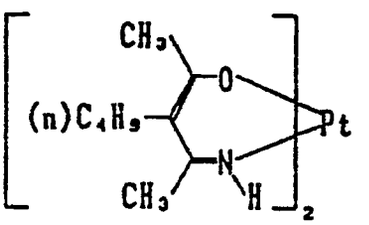

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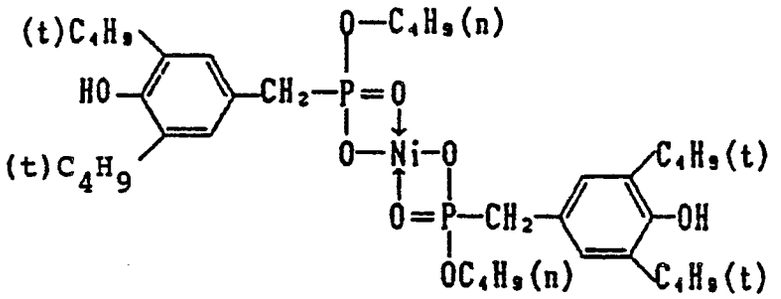

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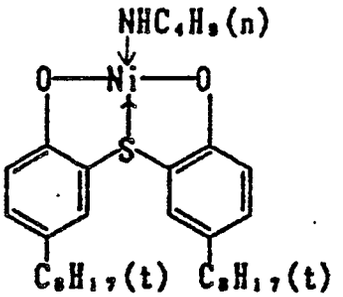

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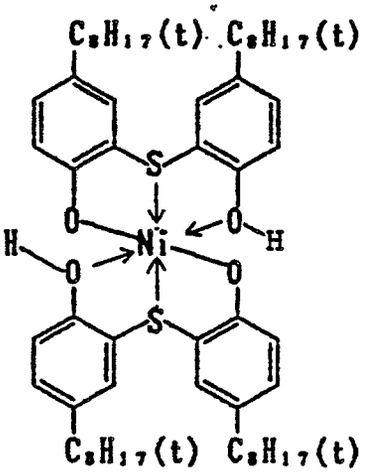


The compounds exemplified above can be prepared using or following the methods described in U.S. Patents 3,336,135, 3,432,300, 3,573,050, 3,574,627, 3,700,455, 3,764,337, 3,935,016, 3,982,944, 4,254,216 and 4,279,990, British Patents 1,347,556, 2,062,888, 2,066,975 and 2,077,455, JP-A-58-205378, JP-A-52-152225, JP-A-53-17729, JP-A-53-20327, JP-A-54-145530, JP-A-55-6321, JP-A-55-21004, JP-A-58-24141, JP-A 59-10539, JP-B-48-31625, and JP-B-54-12337.

The compound represented by formulae (IV) is added in a proportion of from 10 to 400 mol%, preferably from 30 to 300 mol%, to the coupler represented by the general formula (I) or (II-A). The metal complex of formulae (V-1) to (V-4) is added in a proportion of from 1 to 100 mol%, preferably from 3 to 40 mol%, to the coupler represented by the general formula (I) or (II-A).

In incorporating the magenta coupler relating to the present invention and a discoloration inhibitor into a photographic light-sensitive layer, they are first dissolved in a high boiling organic solvent, and then dispersed into at least one hydrophilic organic colloid to constitute the photographic light-sensitive layer.

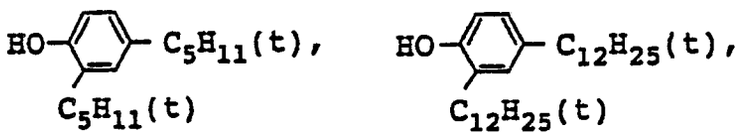
Introduction of couplers into silver halide emulsion layers is generally effected by using known methods as described, e.g., in U.S. Patent 2,322,027.

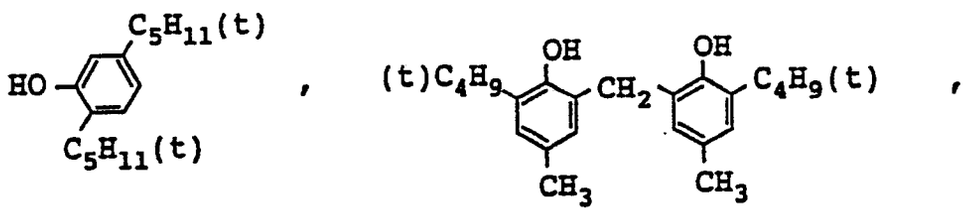
It is preferred that the compound of the present invention is incorporated into a hydrophilic colloid contained in the sensitive material at the stage of the production of the sensitive material. In general, the

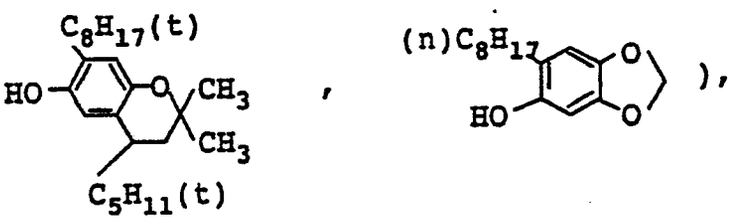
incorporation is effected by dissolving the compound in a high boiling organic solvent with a boiling point of 170°C or above under atmospheric pressure, or a mixed solvent composed of the foregoing oil and a low boiling solvent, and then emulsifying and dispersing the resulting solution in a water solution of a hydrophilic colloid such as gelatin.

Of the compounds of the present invention, those soluble in high boiling solvents (oil) are advantageous. This emulsified dispersion is not particularly restricted as to particle size of oil droplets containing the compounds of the present invention, but the particle size ranges preferably from 0.05 to 0.5μm, more preferably from 0.1 to 0.3 μm.

Specific examples of the foregoing oils include phthalic acid alkyl esters (e.g., dibutyl phthalate, dioctyl phthalate, diisodecyl phthalate, dimethoxyethyl phthalate), phosphoric acid esters (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, dioctyl butyl phosphate, monophenyl-p-t-butylphenylphosphate), citric acid esters (e.g., tributyl acetylcitrate), benzoic acid esters (e.g., octyl benzoate), alkylamides (e.g., diethyllaurylamide, dibutyllaurylamide), fatty acid esters (e.g., dibutoxyethyl succinate, diethyl azelate), trimesic acid esters (e.g., tributyl trimesate), compounds containing an epoxy ring (e.g., compounds described in U.S. Patent 4,540,657), phenols (e.g.,







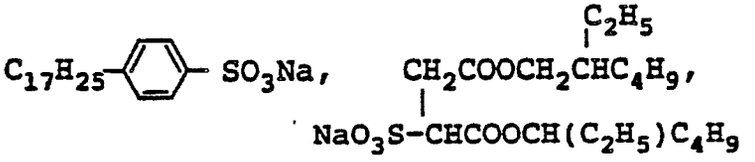
and ethers (e.g., phenoxyethanol, diethylene glycol monophenyl ether). Low boiling solvents used as auxiliary solvents are those having a boiling point ranging from about 30°C to 150°C under atmospheric pressure, with specific examples including lower alkyl acetates such as ethyl acetate, isopropyl acetate and butyl acetate, ethyl propionate, methanol, ethanol, secondary butyl alcohol, cyclohexanol, fluorinated alcohol, methyl isobutyl ketone, β-ethoxyethylacetate, methyl cellosolve acetate, acetone, methyl acetone, acetonitrile, dioxane, dimethylformamide, dimethyl sulfoxide, chloroform, and cyclohexane.

Instead of using high boiling organic solvents, not only oily solvents for additives such as couplers (including those which are solid at room temperature, such as waxes) but also latex polymers can be employed. In addition, the additives themselves, e.g., couplers, color stain inhibitors, ultraviolet absorbents and so on, may serve as oily solvents, too.

As for the latex polymers, those prepared using monomers, such as acrylic acids, methacrylic acids and their esters (e.g., methyl acrylate, ethyl acrylate, butyl methacrylate), acrylamide, t-butylacrylamide, methacrylamide, vinyl esters (e.g., vinyl acetate, vinyl propionate), acrylonitrile, styrene, divinylbenzene, vinyl alkyl ethers (e.g., vinyl ethyl ether), maleic acid esters (e.g., methyl maleate), N-vinyl-2-pyrrolidone, N-vinylpyridine, 1- and 4-vinylpyridines and so on, independently or in combination of two or more thereof can be employed.

Examples of a surface active agent used in dispersing an oily solution, in which the compound of the general formula (I), (II-A), (III) or (IV) is dissolved alone or together with a coupler, into an aqueous protective colloid solution in the present invention, include saponin, sodium alkylsulfosuccinates, and sodium alkylbenzenesulfonates.

Preferably anionic surface active agents having a sulfo group, e.g.,



are used independently or in combination thereof.

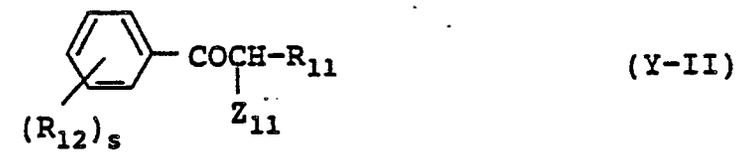
The present invention is not particularly restricted as to other couplers to be used in the color photographic light-sensitive material, and the following couplers can be used.

(a) Yellow Coupler:

Couplers represented by formulae (Y-I) and (Y-II), respectively.

(Y-I)

wherein R_{11} represents a substituted or unsubstituted N-phenylcarbamoyl group, and Z_{11} represents a group capable of splitting off upon the reaction with the oxidation product of an aromatic primary amine developing agent:



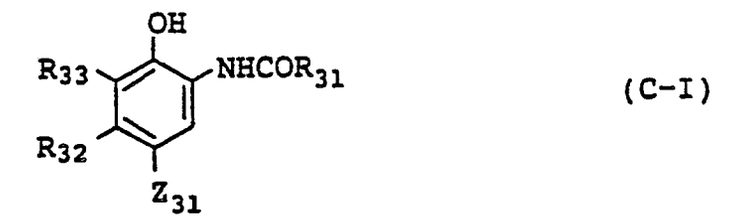
(Y-II)

wherein R_{11} represents a substituted or unsubstituted N-phenylcarbamoyl group, Z_{11} represents a group capable of splitting off in the reaction with the oxidation product of an aromatic primary amine developing agent, R_{12} represents hydrogen or a substituent group, and s is an integer of 1 to 5.

Representative chemical structures of the yellow couplers represented by formulae (Y-I) and (Y-II) include those illustrated in the U.S. Patents 3,894,875 (1-2), 3,408,194 (2-3), 4,404,274 (3-17), 4,022,620 (3-7), 4,057,432 (1-4) wherein the figures in the parentheses indicate the numbers of the columns wherein the foregoing chemical structures are described in detail.

(b) Cyan coupler:

Cyan couplers represented by formula (C-I):



(C-I)

wherein R_{31} represents an alkyl group, a cycloalkyl group, an aryl group, an amino group, or a heterocyclic group; R_{32} represents an acylamino group, or an alkyl group; R_{33} represents hydrogen, halogen, an alkyl group or an alkoxy group, or R_{33} may be linked with R_{32} to form a ring; and Z_{31} represents hydrogen atom,

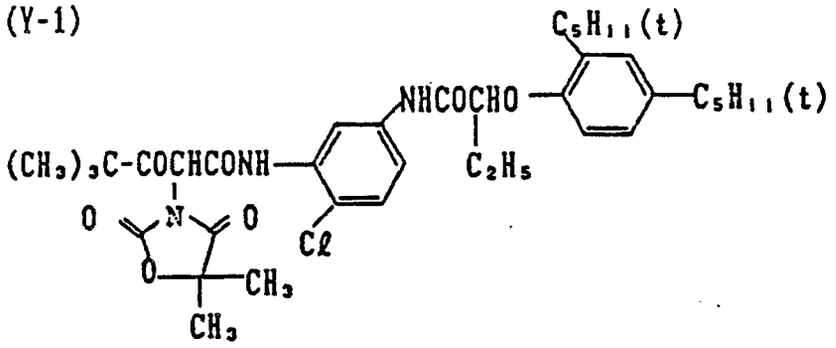
halogen, or a group capable of splitting off in the reaction with the oxidation product of an aromatic primary amine developing agent.

Representative chemical structures of the cyan couples represented by the general formula (C-I) include those illustrated in U.S. Patents 2,920,961 (1), 3,772,002 (1-3), 3,864,366 (2-6), 4,124,396 (2), 4,333,996 (2-8), 4,565,777 (3-5), 4,564,586 (2-4), wherein the figures in the parentheses indicate the numbers of the columns in which the foregoing chemical structures are described in detail.

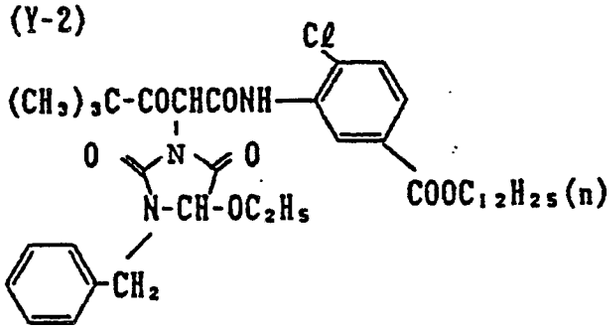
Each of the foregoing couplers may assume the form of a polymer, including a dimer.

Specific examples of these couplers are illustrated below, but the present invention is not to be construed as being limited to the following examples.

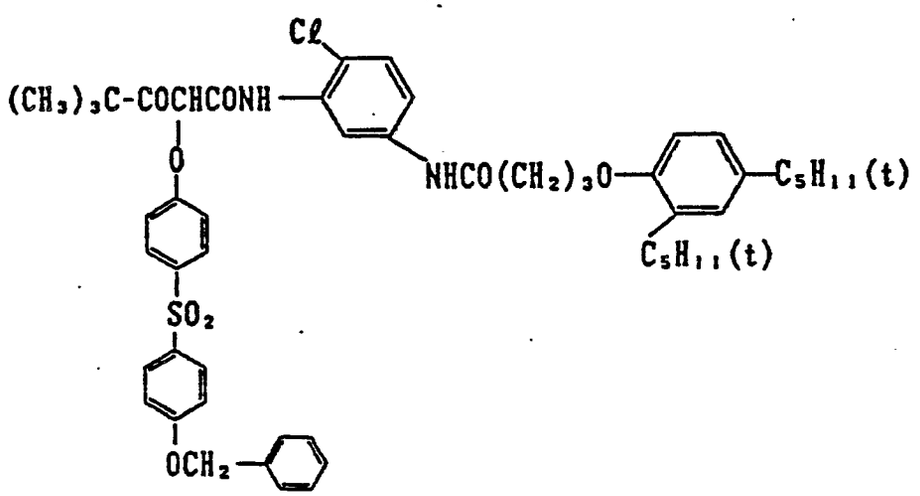
(Y-1)



(Y-2)



(Y-3)



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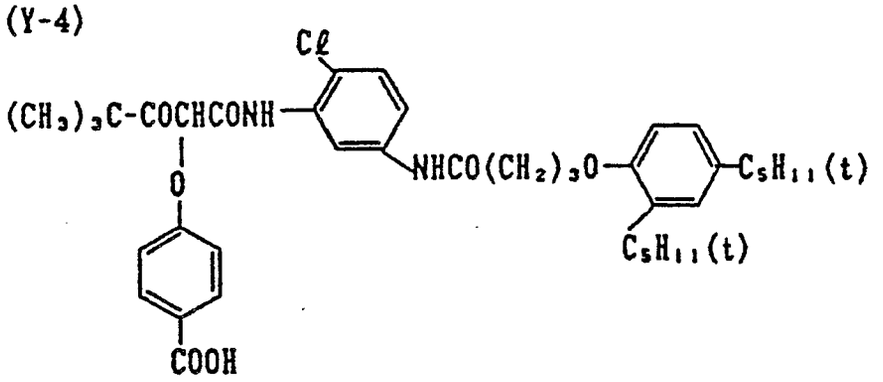

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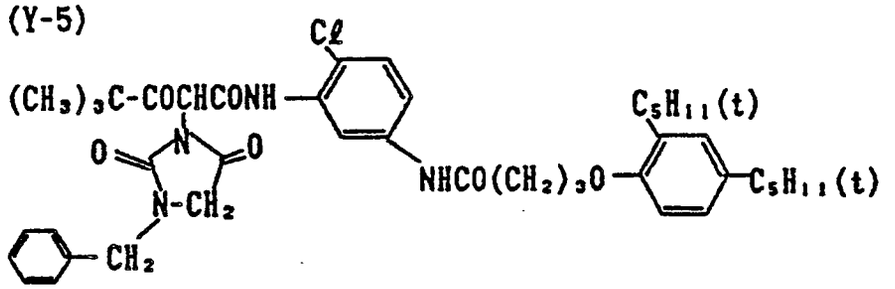

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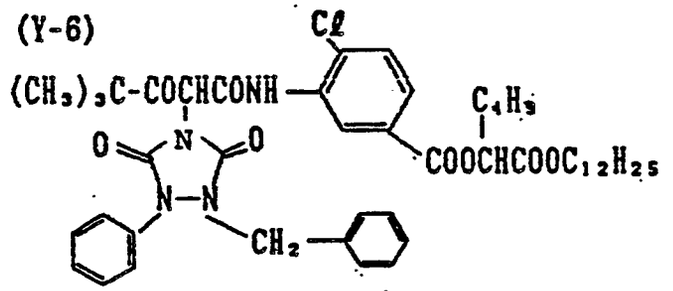

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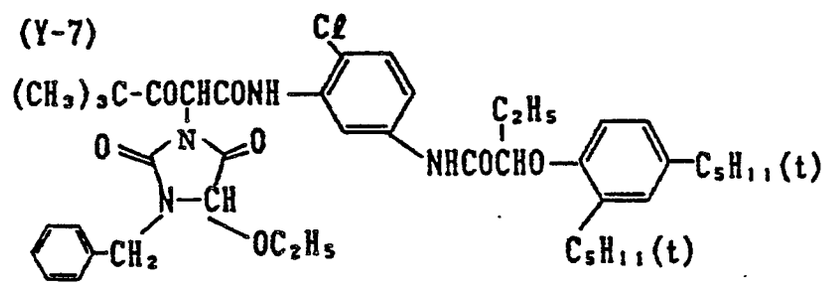

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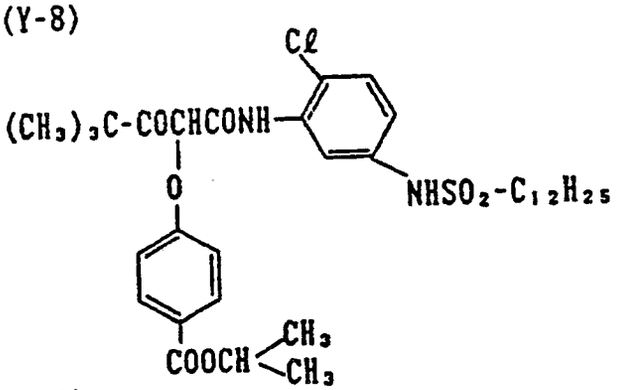

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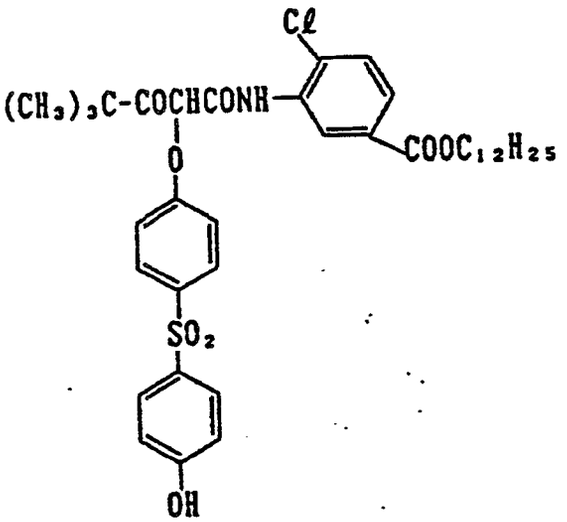

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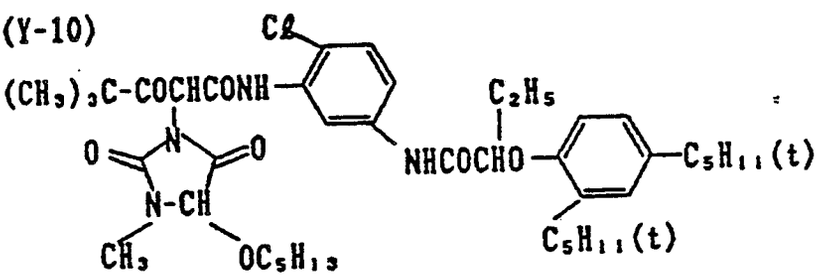

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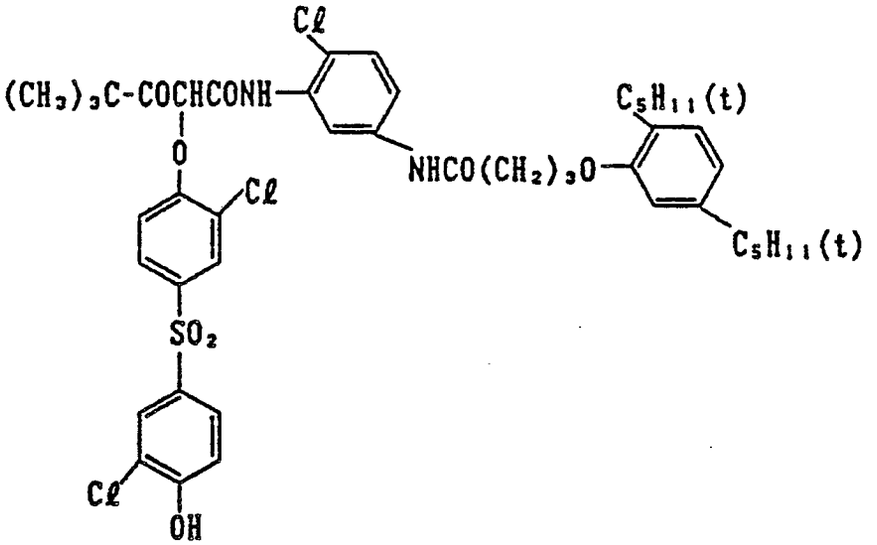

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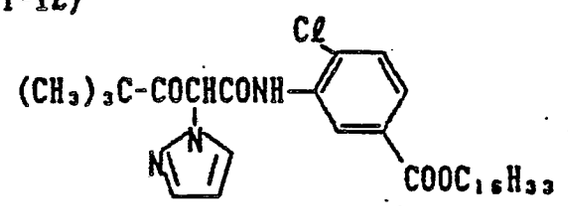

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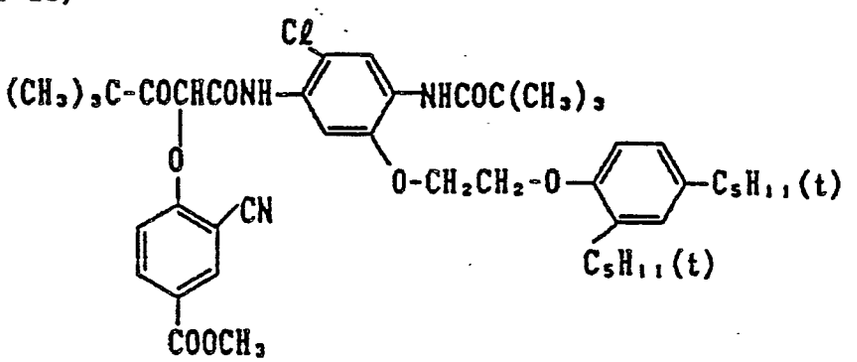

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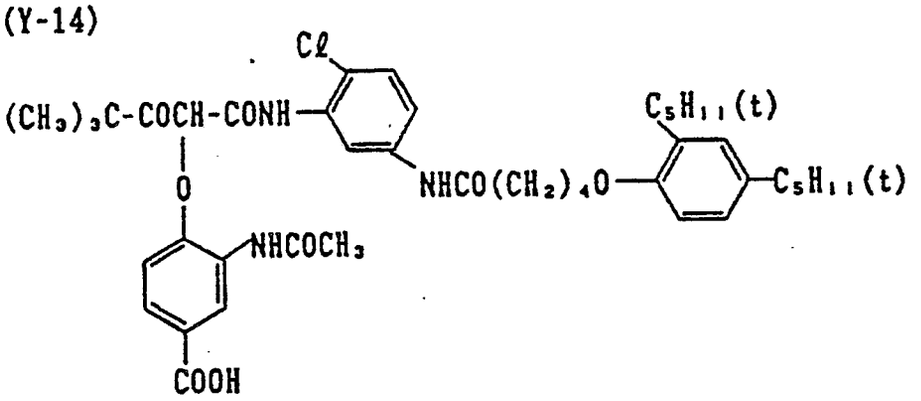

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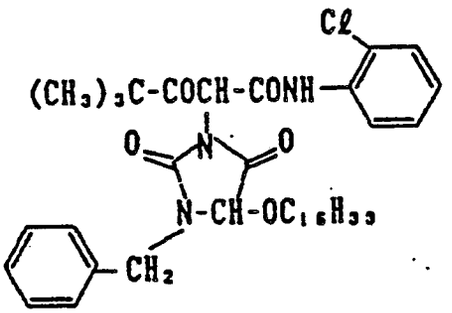

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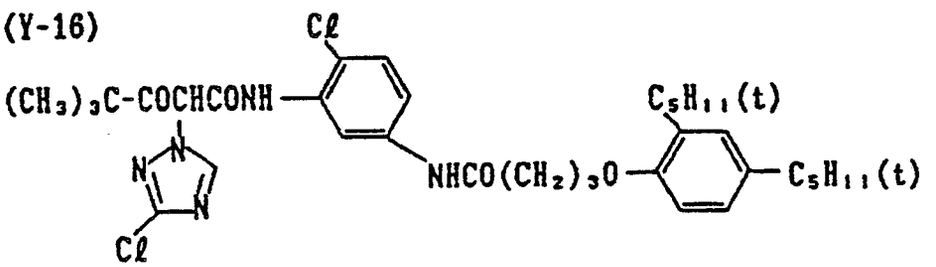

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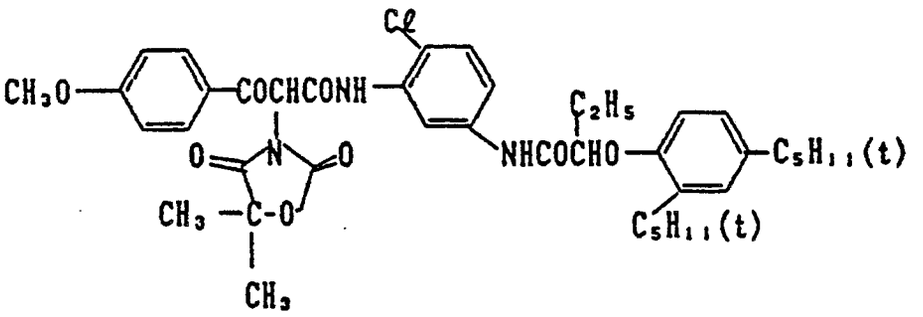

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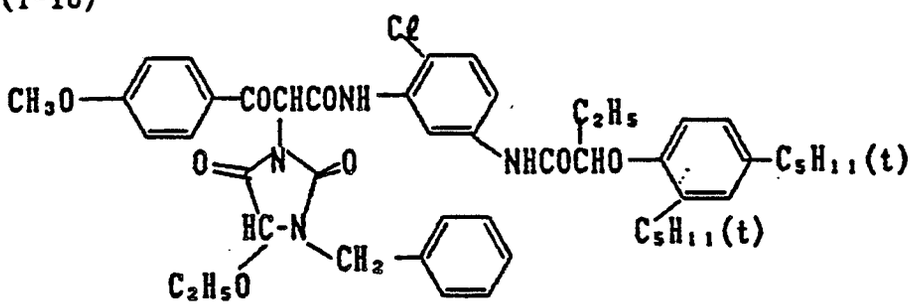

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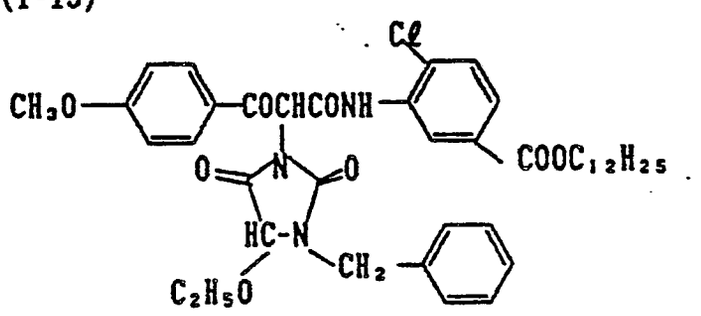

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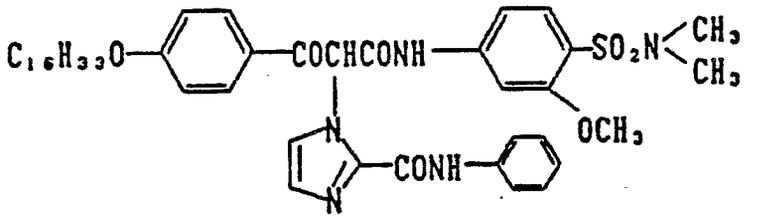

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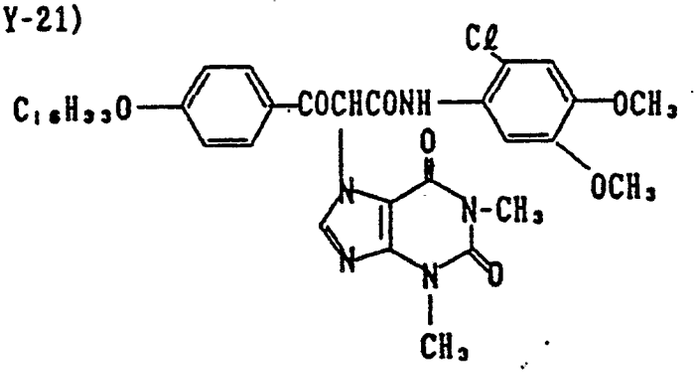

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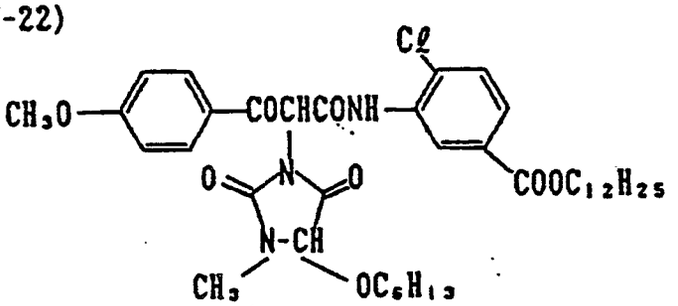

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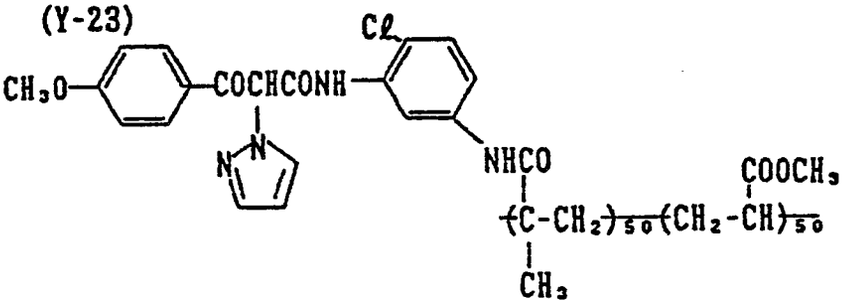

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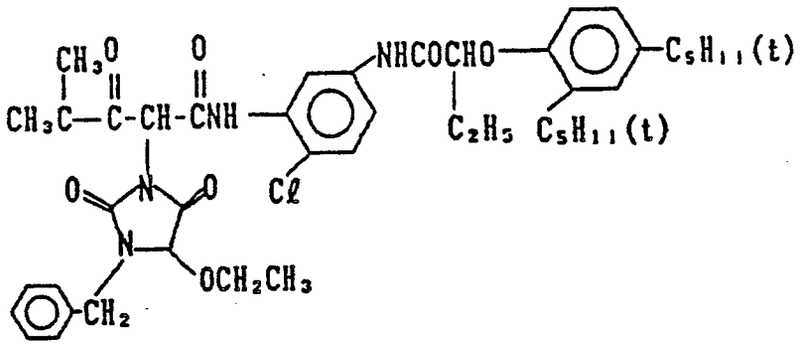

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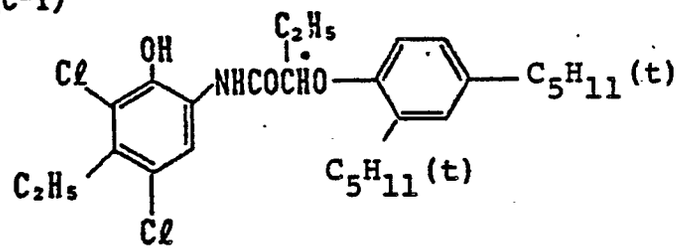

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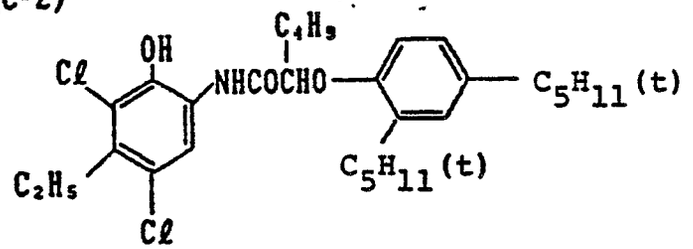

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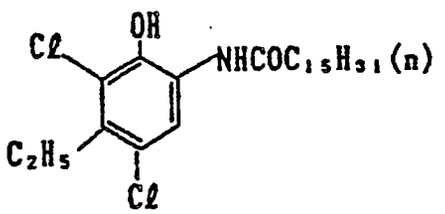

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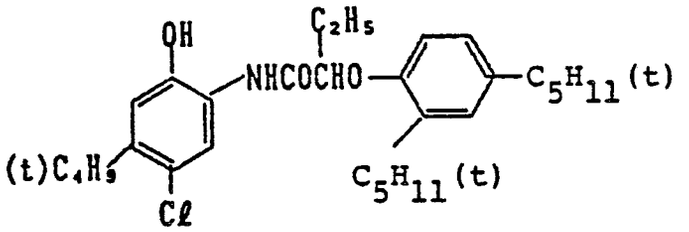

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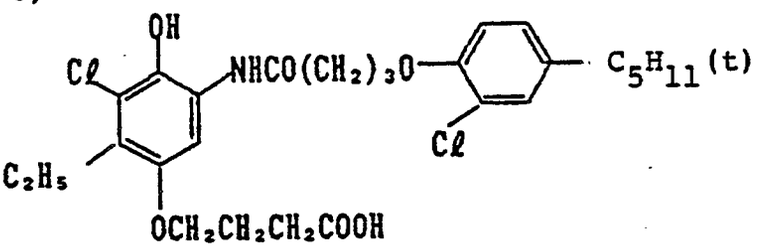

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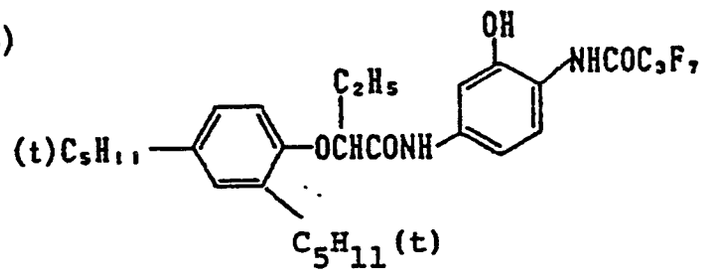

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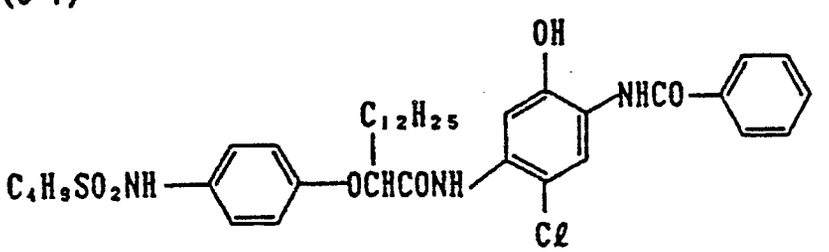

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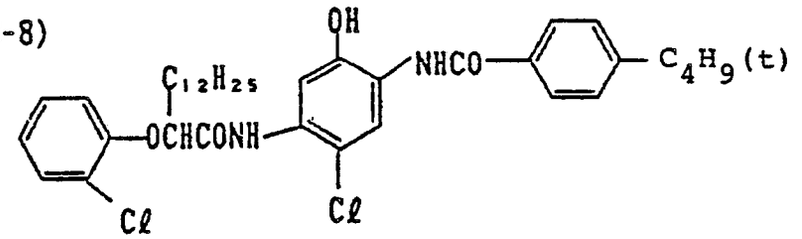

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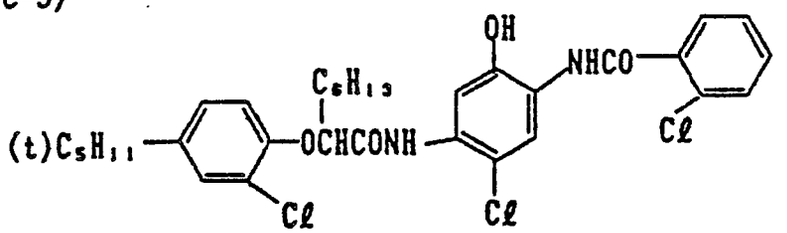

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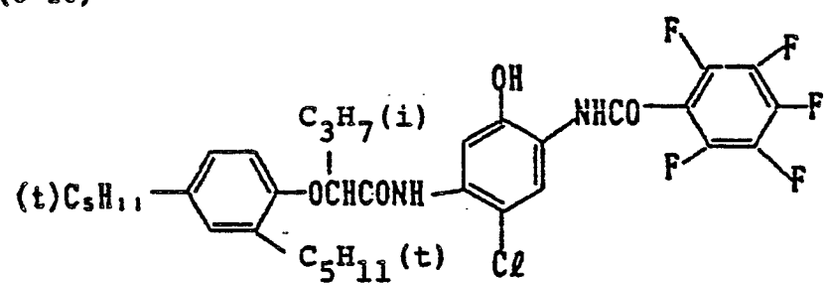

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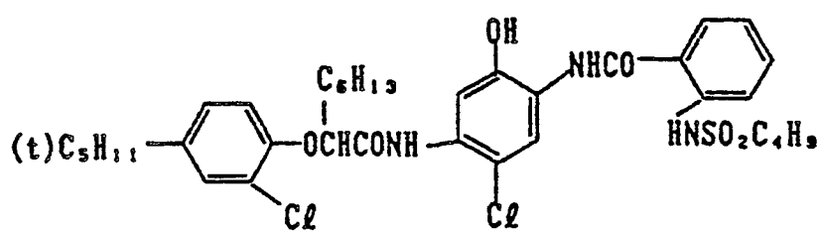

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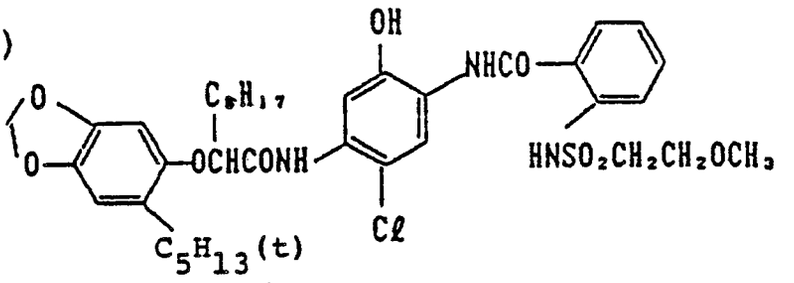

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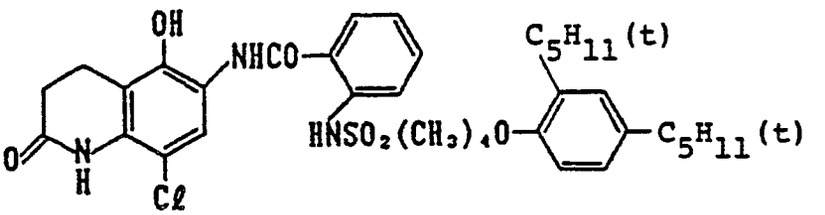

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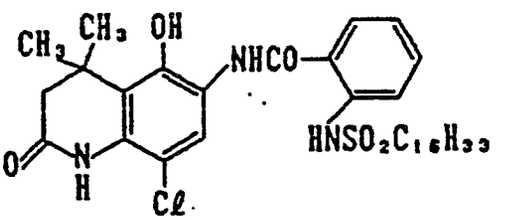

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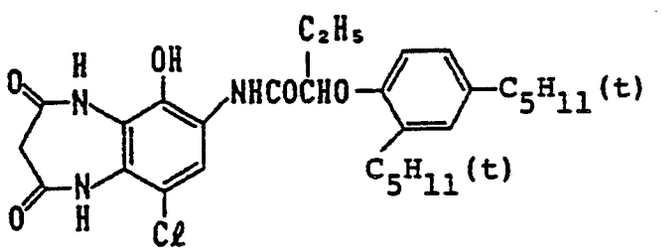

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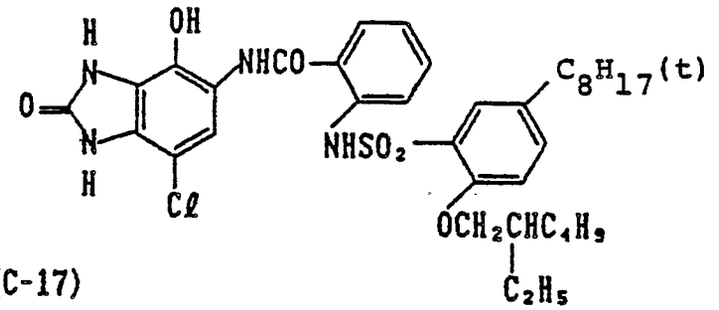

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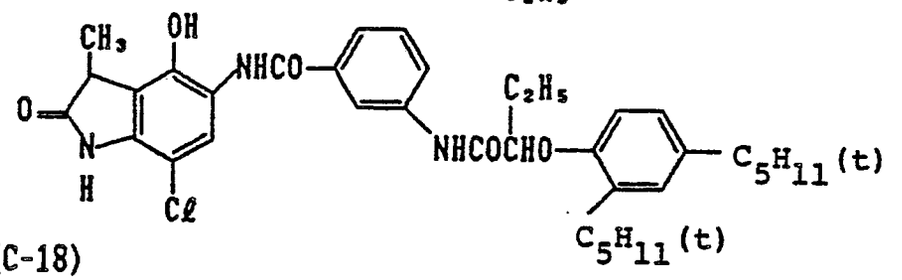

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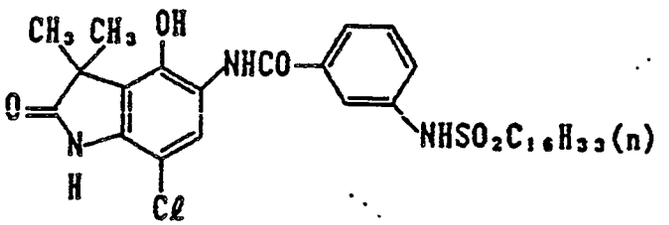

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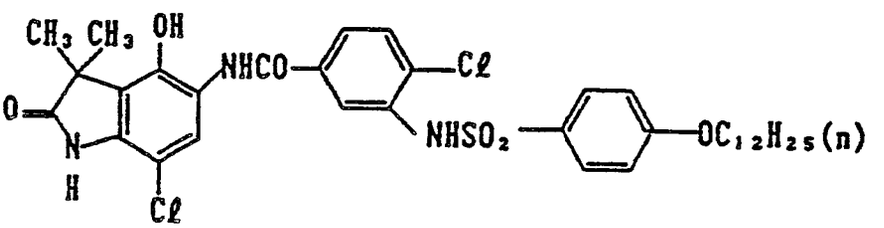

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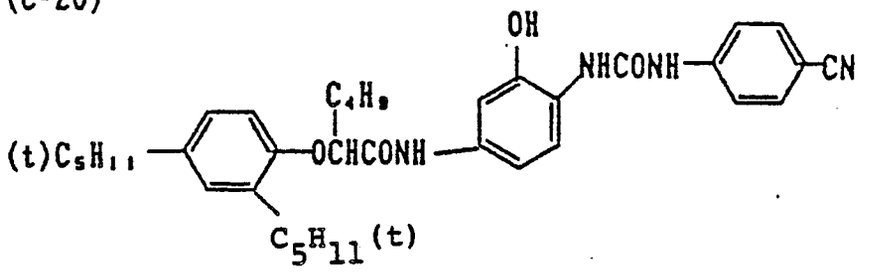

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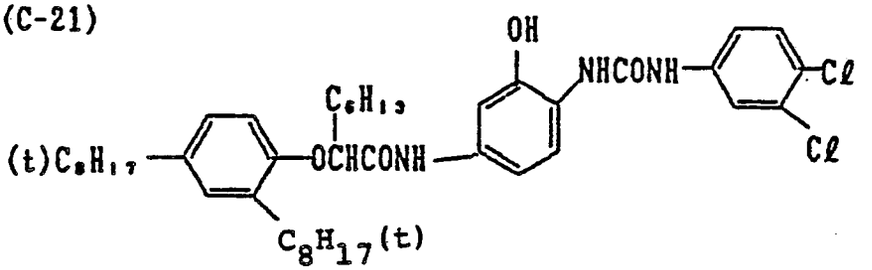

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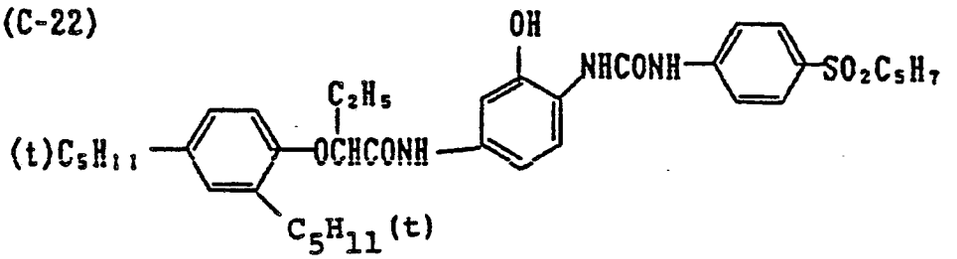

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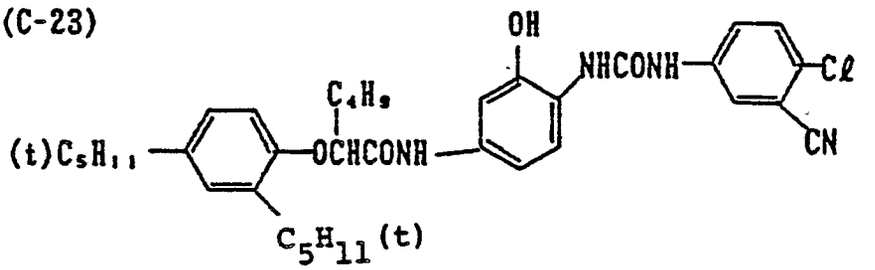

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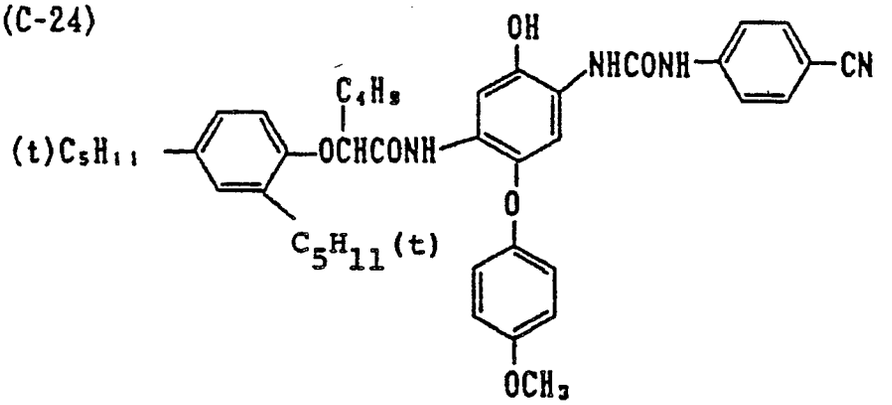

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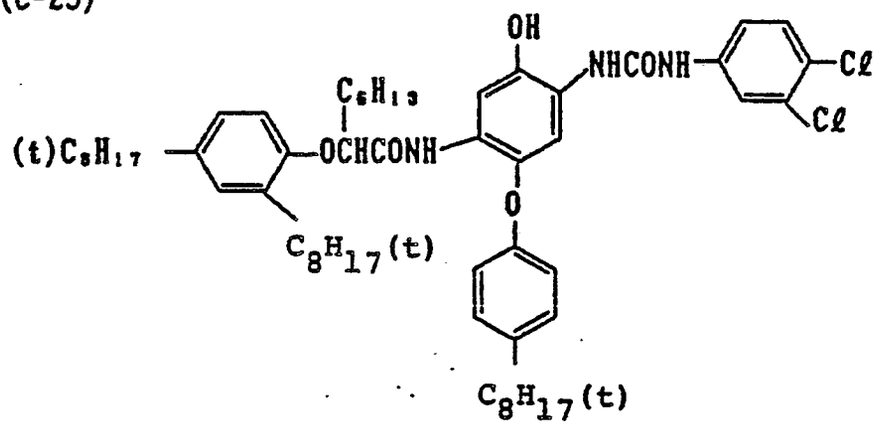

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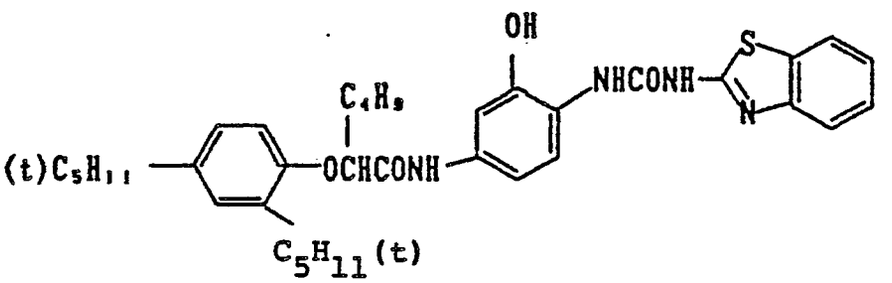

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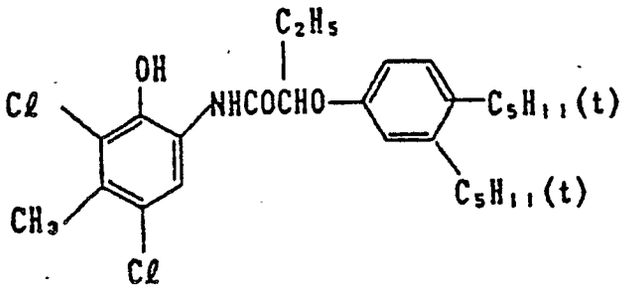

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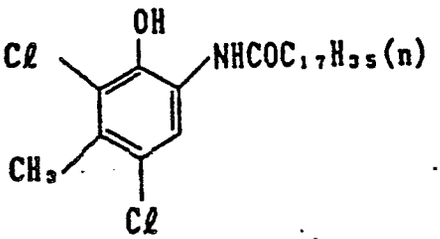

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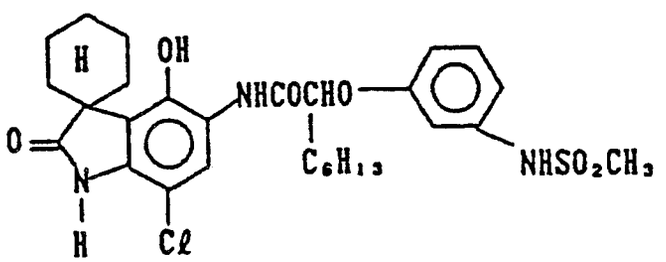


A color developer which can be used in the present invention is described below.

The color developer contains a known aromatic primary amine developing agent. Examples of developing agents which are preferably used are p-phenylenediamine derivatives. Representative examples of such p-phenylenediamine derivatives are cited below. However, the invention is not to be construed as being limited to these examples.

D-1 N,N-Diethyl-p-phenylenediamine
D-2 2-Amino-5-diethylaminotoluene
D-3 2-Amino-5-(N-ethyl-N-laurylamino)toluene
D-4 4-[N-Ethyl-N-(β-hydroxyethyl)amino]aniline
D-5 2-Methyl-4 [N-ethyl-N-(β-hydroxyethyl)amino]aniline
D-6 4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]aniline
D-7 N-(2-Amino-5-diethylaminophenylethyl)methanesulfonamido
D-8 N,N-Dimethyl-p-phenylenediamine
D-9 4-Amino-3-methyl-N-ethyl-N-methoxyethylaniline
D-10 4-Amino-3-methyl-N-ethyl-N-β-ethoxyethylaniline
D-11 4-Amino-3-methyl-N-ethyl-N-β-butoxyethylaniline

Of the above p-phenylenediamine derivatives, 4-amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)-

ethyl] aniline (exemplified compound D-6) is particularly preferred.

These p-phenylenediamine derivatives may assume the form of a salt, such as sulfate, hydrochloride, sulfite, p-toluenesulfonate, or so on. A preferred amount of the aromatic primary amine developing agent added to 1 liter of a developer ranges from about 0.1 g to about 20 g, particularly from about 0.5 g to about 10 g.

To the color developer, a sulfite such as potassium sulfite, sodium hydrogen sulfite, potassium hydrogen sulfite, sodium metasulfite, potassium metasulfite, or a carbonyl/sulfinic acid adduct can be added, if needed.

In addition, various hydroxylamines, hydroxamic acids disclosed in JP-A-63-43138, hydrazines and hydrizides disclosed in Japanese Patent Application No. 61-170756, phenols disclosed in JP-A-63-44657 and JP-A-63-58443, α-hydroxyketones and α-aminoketones disclosed in JP-A-63-44656, and/or various sugars disclosed in JP-A-63-36244 may be added for the purpose of directly preserving the above-described color developing agents. Moreover, the combined use of the above-described compounds with monoamines disclosed in JP-A-63-4235, JP-A-63-24254, JP-A-63-21647, Japanese Patent Application No. 1164515/86, JP-A-63-27841 and JP-A-63-25654, diamines disclosed in JP-A-63-30845, Japanese Patent Application No. 61-164515, and JP-A-63-43139, polyamines disclosed in JP-A-63-21647 and JP-A-63-26655, polyamines disclosed in JP-A-63-44655, nitroxy radicals disclosed in JP-A-63-53551, alcohols disclosed in JP-A-63-43140 and JP-A-63-53549, oximes disclosed in JP-A-63-56654, and/or tertiary amines disclosed in Japanese Patent Application No. 61-265149 is advantageous.

As other preservatives, the developer may contain various metals disclosed in JP-A-57-44148 and JP-A-57-53749, salicylic acids disclosed in JP-A-59-180588, alkanolamines disclosed in JP-A-54-3532, polyethyleneimines disclosed in JP-A-56-94349, and aromatic polyhydroxy compounds disclosed in U.S. Patent 3,746,544, if desired. In particular, the addition of the aromatic polyhydroxy compounds is preferred.

The color developer used in the present invention is adjusted to a pH of 9 to 12, preferably a pH of 9 to 11.0. In addition to the above-described ingredients, the color developer can contain other known compounds as developer components.

For the purpose of maintaining the foregoing pH, it is preferred that various buffering agents should be used. Specific examples of buffering agents include sodium carbonate, potassium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, trisodium phosphate, tripotassium phosphate, disodium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfosalicylate), and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate). However, the invention is not to be construed as being limited to these compounds.

The amount of the buffering agents to be added to the color developer is preferably 0.1 mol/ℓ or more, particularly from 0.1 to 0.4 mol/ℓ.

In addition, various kinds of chelating agents may be contained in the color developer in order to prevent calcium and magnesium from precipitating, or in order to enhance the stability thereof.

Specific examples of chelating agents which can be used are cited below, but the invention is not to be construed as being limited to such examples.

Specifically, they include nitrilotriacetic acid, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid, N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N′,N′-tetramethylenephosphonic acid, transcyclohexanediaminetetraacetic acid, 1,2-di aminopropanetetraacetic acid, glycoletherdiaminetetraacetic acid, ethylenediamine-o-hydroxyphenylacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, and N,N′-bis(2-hydroxybenzyl)-ethylenediamine-N,N′-diacetic acid.

These chelating agents may be used in a combination of two or more thereof, if needed.

These chelating agents can be added in any amount sufficident to mask metal ions in the color developer. For instance, they may be added in an amount of 0.1 to 10 g per liter of the color developer.

The color developer can contain any development accelerator, if needed.

Development accelerators can produce a particularly remarkable effect in the present invention when a color developer which is substantially free from benzyl alcohol is used.

Specifically, thioether compounds disclosed in JP-B-37-16088, JP-B-37-5987, JP-B-38-7826, JP-B-44-12380, JP-B-45-9019 and U.S. Patent 3,813,247; p-phenylenediamine compounds disclosed in JP-A-52-49829 and JP-A-50-15554; quaternary ammonium salts disclosed in JP-A-50-137726, JP-B-44-30074, JP-A-56-156826 and JP-A-52-43429; amine compounds disclosed in U.S. Patents 2,494,903, 3,128,182, 4,230,796 and 3,253,919, JP-B-41- 11431, and U.S. Patents 2,482,546 and 2,596,926; polyalkyleneoxides disclosed in JP-B-37-16088, JP-B-42-25201, U.S. Patent 3,128,183, JP-B-41-11431, JP-B-42-23883 and

U.S. Patent 3,532,501; 1-phenyl-3-pyrazolidones, and imidazoles can be added as a development accelerator, if desired.

The color developer used in the present invention can contain any antifoggant, if desired. Suitable examples of antifoggants which can be used include alkali metal halides such as sodium chloride, potassium bromide and potassium iodide, and organic antifoggants. Typical examples of organic antifoggants include nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chloro-benzotriazole, 2-thiazolyl-benzimidazole, 2-thiazolylmethyl-benzimidazole, indazole, hydroxyazaindolizine, and adenine.

Further, the color developer to be used in the present invention preferably contains a brightening agent. Suitable brightening agents are 4,4′ diamino-2,2′-disulfostilbene type compounds, and a preferred addition amount thereof ranges from 0 to 5 g/ℓ, particularly from 0.1 to 4 g/ℓ.

Furthermore, the color developer may contain various kinds of surface active agents such as alkylsulfonic acids, arylsulfonic acids, aliphatic carboxylic acids and aromatic carboxylic acids, if desired.

The processing using the color developer of the present invention is performed at a temperature ranging from 20° C to 50° C, preferably from 30° C to 40° C. The time of the processing ranges from 20 seconds to 5 minutes, preferably from 30 seconds to 2 minutes. It is preferred that a replenisher is added in a smal amount, of from 20 to 600 ml, preferably from 50 to 300 ml, and more preferably from 100 ml to 200 ml, per square meter of the sensitive material processed.

A desilvering step performed in the present invention is described in detail below.

In the desilvering step of the present invention, a bleach-fix bath is used. The effect of the present invention becomes more remarkable the shorter a desilvering time is. More specifically, the desilvering time is 6 minutes or shorter, preferably between 30 seconds and 4 minutes, more preferably between 30 seconds and 60 seconds.

A bleach-fix bath which can be used in the present invention is described in detail below.

Examples of a bleaching agent which can be used in the bleach-fix bath of the present invention include organic complex salts of iron, cobalt, nickel, manganese and chromium. In particular, organic complex salts formed by Fe(III) and aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid, and diethylenetriaminepentaacetic acid, aminopolyphosphonic acids, phosphonocarboxylic acids, organic phosphonic acids, citric acid, tartaric acid, and malic acid, are preferred.

Of these bleaching agents, aminopolycarboxylic acid complex salts of Fe(III) are particularly preferred for rapid processing and prevention of environmental pollution. Examples of useful aminopolycarboxylic acids for forming the organic complex salts include ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, 1,3-diaminopropanetetraacetic acid, propylenediaminetetraacetic acid, nitrilotriacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, iminodiacetic acid, and glycoletherdiaminetetraacetic acid. These compounds may assume the form of a sodium, potassium, lithium or ammonium salt. Of these bleaching agents, (ethylenediaminetetraacetato)iron(III), (diethylenetriaminepentaacetato)iron(III), (cyclohexanediaminetetraacetato)iron(III), (1,3-diaminopropanetetraacetato)iron (III) and (methyliminodi acetato)iron(III) complexes are preferred for high bleaching power.

These ferric ion complexes may be used in the form of complex salts, or may be formed in the bath by adding thereto both ferric salts, such as ferric sulfates, ferric chloride, ammonium ferric sulfate, and ferric phosphate, and chelating agents of aminopolycarboxylic acid type. Moreover, these chelating agents may be used in excess of amounts required for forming the ferric ion complexes. A suitable amount of the foregoing bleaching agent added ranges from 0.01 to 1.0 mole, preferably from 0.05 to 0.50 mole, per liter of the bath.

The bleach-fix bath and/or the pre-bath thereof can contain various compounds as a bleach accelerator. Examples of bleach accelerators which are preferred for great accelerating effect include the compounds containing a mercapto group or a disulfide linkage, described in U.S. Patent 3,893,858, German Patent 1,290,812, JP-A-53-95630 and Research Disclosure, No. 17129 (July 1978), thiourea compounds disclosed in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735 and U.S. Patent 3,706,561, and halogen ions such as iodide and bromide.

In addition, the bleach-fix bath used in the present invention can contain a rehalogenating agent such as bromides (e.g., potassium bromide, sodium bromide, ammonium bromide), chlorides (e.g., potassium chloride, sodium chloride, ammonium chloride), or iodides (e.g., ammonium iodide). Further, it can contain one or more of an inorganic or organic acid, an alkali metal or ammonium salt thereof, which has a pH buffering ability, such as boric acid, borax, sodium metaborate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorous acid, phosphonic acid, sodium phosphate, citric acid, sodium citrate, tartaric acid, and a corrosion inhibitor such as ammonium nitrate, or guanidine.

Fixers which can be preferably used in the bleach-fix bath include known thiosulfates such as sodium thiosulfate, and ammonium thiosulfate. Also, a special bleach-fix bath which contains, e.g., a combination of a fixer with a large amount of a halide such as potassium iodide described in JP-A-55-155354 can be employed. The amount of the fixer added ranges from 0.3 to 2 moles, preferably from 0.5 to 1.0 mole, per liter of the bath.

The bleach-fix bath of the present invention is adjusted to a pH of 3.5 to 6.5, preferably 4 to 5.5. For the purpose of adjusting the pH to the foregoing range, various kinds of organic or inorganic acids, bases and buffering agents can be used. Specific examples of acids include hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, acetic acid, propionic acid, and citric acid, and alkalis include sodium hydroxide, potassium hydroxide, aqueous ammonia, and various amines. The invention is not to be construed as being limited to these examples.

When the pH of the bleach-fix bath is higher than the above-described range, the bath is inferior in desilvering power and provides images inferior in stability, whereas when the bath has a lower pH than the above-described range it suffers from deterioration of stability, and converts the cyan dyes produced to their corresponding leuco bodies to a considerable extent.

Also, the bleach fix bath may contain various kinds of brightening agents, defoaming agents, surface active agents, polyvinyl pyrrolidone, and organic solvents such as methanol.

The bleach-fix bath and a fixing bath which can be used in the present invention can contain as a preservative a sulfinic acid ion releasing compound, such as sulfites (e.g., sodium sulfite, potassium sulfite, ammonium sulfite), hydrogen sulfites (e.g., ammonium hydrogen sulfite, sodium hydrogen sulfite, potassium hydrogen sulfite), and metabisulfites (e.g., potassium metabisulfite, sodium metabisulfite, ammonium metabisulfite). Such a compound is preferably added in an amount of about 0.02 to 0.50 mol/ℓ, particularly 0.04 to 0.40 mol/ℓ, on a sulfinic acid ion basis.

Though sulfites are generally used as preservative, other preservatives such as ascorbic acid, adducts of carbonyl compounds and bisulfites, and carbonyl compounds may be added.

Further, buffering agents, brightening agents, chelating agents, defoaming agents, and antimolds may optionally be added.

After the desilvering step, such as the fixing or the combined bleaching and fixing step, the silver halide color photographic material of the present invention is, in general, subjected to a washing step and/or a stabilizing step.

The volume of washing water required can be determined depending on the characteristics of photosensitive materials to be processed (e.g., the kind of couplers incorporated therein), end-use purposes of photosensitive materials to be processed, the temperature of washing water, the number of washing tanks (stage number), the method of replenishing washing water (e.g., whether a current of water flows in the countercurrent direction, or not), and other conditions. Of these conditions, the relation between the number of washing tanks and the volume of washing water in the multistage countercurrent process can be determined according to the methods described in Journal of the Society of Motion Picture and Television Engineers, volume 64, pages 248 to 253 (May 1955). A preferred step number in the multistage countercurrent process is generally from 2 to 6, particularly from 2 to 4.

According to the multistage countercurrent process, the volume of washing water can be sharply reduced. For instance, it becomes feasible to decrease it to 0.5 to 1 liter per square meter of the sensitive material processed. However, the process has disadvantages, e.g., in that bacteria propagate in the tanks because of the increase in staying time of water in the tanks, and suspended matter produced from the bacteria sticks to photosensitive materials processed therein. In the processing of the color photosensitive material of the present invention, the method of reducing the contents of calcium and magnesium, which is disclosed in JP-A-62-288838, can be employed to great advantage for solving the above-described problem. Further, bactericides such as isothiazolone compounds and thiabendazoles disclosed in JP-A-57-8542, chlorine-containing germicides such as a sodium salt of chlorinated isocyanuric acid, benzotriazoles disclosed in JP-A-61-267761, copper ion, and other germicides described in Hiroshi Horiguchi, Bohkin Bohbai Zai no Kagaku (which means "Chemistry of Antibacteria and Antimolds"), Biseibutsu no Mekkin Sakkin Bohbai Gijutsu (which means "Arts of Sterilizing and Pasteurizing Microbe and Proofing Against Mold"), compiled by Eisei Gijutsu Kai, and Bohkin- and Bohbai-zai Jiten (which means "Thesaurus of Antibacteria and Antimolds"), comEpiled by Nippon Bohkin Bohbai Gakkai.

In addition, the washing water can contain a surface active agent as a draining agent, and a chelating agent represented by EDTA as a water softener.

Washing water to be used in the processing of the photosensitive material of the present invention is adjusted to pH 4 to 9, preferably to pH 5 to 8. The washing temperature and a washing time, though can be chosen varied depending on the characteristics and the intended use of the photosensitive material to be

washed, and are generally in a range of 20 sec. to 10 min. at 15° C to 45° C, preferably 30 sec. to 5 min. at 25° C to 40° C.

After the above-described washing step, or without any washing step, the photosensitive material of the present invention is processed with a stabilizing bath. To the stabilizing bath are added compounds having an image-stabilizing function, such as aldehyde compounds represented by formaldehyde, buffering compounds for adjusting the film pH to a value suitable for stabilization of the produced dyes, and ammonium compounds. In addition, the stabilizing bath can contain the above described various bactericides and antimolds for the purposes of prevention of propagation of bacteria in the bath, and imparting an antimolding ability to the sensitive materials processed thereby.

Further, surface active agents, brightening agents and hardeners may be added to the stabilizing bath.

When the sensitive material of the present invention is directly subjected to the stabilization step without experiencing any washing step, any known methods described in JP-A-57-8543, JP-A-58-14834, JP-A-59-184343, JP-A-60-220345, JP-A-60-238832, JP-A-60-239784, JP-A-60-239749, JP-A-61-4054 and JP-A-61-118749, can be applied to the stabilization step of the present invention.

Also, it is preferred to additionally add chelating agents such as 1-hydroxyethylene-1,1-diphosphonic acid, ethylenediaminetetramethylenephosphonic acid, magnesium compounds and bismuth compounds.

Solutions used in the washing and/or the stabilization step can be further used in the pre-step. For instance, washing water overflowing the washing bath, which has been reduced in volume by using a multistage countercurrent process, is conducted into the prebath, that is, the bleach-fix bath, and the bleach-fix bath is replenished with a concentrated solution to achieve the reduction of waste solutions.

The silver halide color photographic material of the present invention can be applied to color paper, color reversal paper, direct-positive color photographic materials, color positive films, color negative films, color reversal films, and so on. In particular, when applied to color paper and color reversal paper, the present invention can produce desirable effects.

In the silver halide emulsions of the sensitive material of the present invention, any silver halide, including silver iodobromide, silver bromide, silver chlorobromide, and silver chloride can be used. More specifically, a silver chlorobromide emulsion having a chloride content of 60 mol% or more, especially 80 mol% or more, and a silver chloride emulsion are preferred in the case of, e.g., color paper, wherein a rapid processing or a low replenishment processing is carried out. On the other hand, a silver chlorobromide emulsion having a bromide content of 50 mol% or more, especially 70 mol% or more, and a silver bromide emulsion (which each may have an iodide content of 3 mol% or less) are preferred when high sensitivity is needed, and it is necessary to suppress the generation of fog at the time of producing, preserving and/or processing the sensitive material. In the case of color photographic materials for photograph-taking use, silver iodobromide emulsions and silver chloroiodobromide emulsions, each having an iodide content of 3 to 15 mol%, are preferably used.

The silver halide grains, may have a multi-phase structure, such that the interior and the surface of the grains may differ or the grains may have a junction structure, or the silver halide grains may be uniform throughout. In particular, a double layer structure is preferred. Also, various structures may be present together.

The size distribution of the silver halide grains to be used in the present invention, may be narrow or broad, and is preferably of "monodisperse". The term "monodisperse" system as used herein refers to a dispersion system in which the value obtained by dividing the standard deviation (from the size distribution curve of the silver halide emulsion grains) by the average grain size (variation coefficient) is below 20%, preferably below 15%. In order to satisfy the desired gradation, two or more monodisperse silver halide emulsions (preferably having their respective variation coefficient in the above-described range), which have substantially the same color sensitivity, but different grain size, or plural kinds of grains having the same size but different sensitivities can be coated as a mixture in the same layer, or separately in superposed layers. In addition, a combination of two or more of polydisperse silver halide emulsions, or a combination of monodisperse and polydisperse emulsions can be used as a mixture, or coated separately in superposed layers.

The silver halide grains to be used in the present invention may have a regular crystal form, such as a cube, an octahedron, a rhombic dodecahedron, or a tetradecahedron. Grains having different regular crystal forms may be present as a mixture. They also may have an irregular crystal form, such as a sphere. Also, the grains may have a composite form of the above-described forms.

Of these crystal forms, a cubic form and a tetradecahedral form are particularly preferred in the present invention.

Moreover, the silver halide emulsion grains may assume a tabular form, particularly having a length/thickness ratio of from 5 to 8. In addition, emulsion wherein 50% or more (on a projection area basis)

of the grains assume a tabular form having a length/thickness ratio of 8 or more may be used. Also, a mixture of emulsion grains having these various crystal forms may be used.

These various emulsions may form a latent image predominantly at the surface of the grains, or may mainly form a latent image inside the grains.

The photographic emulsions used in the present invention can be prepared using the methods described in Research Disclosure, vol. 176, Item No. 17643 (I, II, III) (Dec. 1978).

The emulsions used in the present invention are generally ripened physically and chemically, and further sensitized spectrally. Additives used in these steps are described in Research Disclosure, Vol. 176, No. 17643 (Dec. 1978) and Vol. 187 No. 18716 (Nov. 1979) as set forth in the following table.

Photographic additives which can be used in the present invention are also described in these two publications, as summarized in the following table.

Additives	RD 17643	RD 18716
1. Chemical sensitizers	p. 23	p. 648, right column
2. Sensitivity-increasing agents		"
3. Spectral sensitizers	p. 23-24	p. 648, right column
4. Supersensitizers		p. 649, right column
5. Brightening agents	p. 24	
6. Antifoggant and Stabilizers	p. 24-25	p. 649, right column
7. Couplers	p. 25	
8. Organic solvents	p. 25	
9. Light absorbers, Filter dyes, and UV-ray absorbers	p. 25-26	p. 649, right column to p. 650, left column
10. Stain inhibitor	p. 25, right column	p. 650, left column to right column
11. Dye image-stabilizing agents	p. 25	
13. Hardeners	p. 26	p. 651, left column
14. Binders	p. 26	"
15. Plasticizers and Lubricants	p. 27	p. 650, right column
16. Coating aids and Surface active agents	p. 26-27	"
17. Antistatic agents	p. 27	"

EXAMPLE 1

On a paper support laminated with a polyethylene film on both sides thereof, were coated the layers described below in this order to prepare a multilayer silver halide light-sensitive material. Coating compositions were prepared in the following manner.

Preparation of Coating Composition for First Layer:

To a mixture of 10.2 g of a yellow coupler (ExY-1), 9.1 g of a yellow coupler (ExY-2) and 4.4 g of a color image stabilizer (Cpd-1), were added 27.2 ml of ethyl acetate and 7.7 ml (8.0 g) of a high boiling solvent (Solv-1) to make a solution. The solution was emulsified and dispersed in 185 ml of a 10% aqueous gelatin solution containing 8 ml of a 10% sodium dodecylbenzenesulfonate solution. The resulting emulsified dispersion was mixed homogeneously with the emulsions EMI and EM2, and further the gelatin concentration therein was adjusted so that the resulting emulsion had the composition described below. Thus, the coating composition for the first layer was prepared.

Coating compositions for the second to the seventh layers were prepared in the same manner as that for the first layer. In each layer, sodium salt of 1-hydroxy-3,5-dichloro-s-triazine was contained as gelatin hardener. In addition, Cpd-2 was used as viscosity increasing agent.

Constituent Layers:

The ingredients used and their coverages expressed in terms of g/m^2 are described below, with the coverage of silver halide expressed on a silver basis.

Support

Polyethylene-laminated paper (containing a white pigment (TiO_2) and a bluish dye on the first layer side).

First Layer (Blue-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM1) sensitized spectrally with a blue sensitizing dye (ExS-1)	0.13
Monodisperse silver chlorobromide emulsion (EM2) sensitized spectrally with a blue sensitizing dye (ExS-1)	0.13
Gelatin	1.86
Yellow coupler (ExY-1)	0.44
Yellow coupler (ExY-2)	0.39
Color image stabilizer (Cpd-1)	0.19
Solvent (Solv-1)	0.35

Second layer (Color stain inhibiting layer)

Gelatin	0.99
Color stain inhibitor (Cpd-3)	0.08

Third layer (Green-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM3) sensitized spectrally with green sensitizing dyes (ExS-2, ExS-3)	0.05
Monodisperse silver chlorobromide emulsion (EM4) sensitized spectrally with green sensitizing dyes (ExS-2, ExS-3)	0.11
Gelatin	1.80
Magenta coupler (ExM-1)	0.39
Color image stabilizer (Cpd-5)	0.01
Color image stabilizer (Cpd-6)	0.04
Solvent (Solv-2)	0.12
Solvent (Solv-3)	0.25

Fourth Layer (Ultraviolet absorbing layer)

Gelatin	1.60
Ultraviolet absorber (Cpd-7/Cpd-8/Cpd-9 = 3/2/6 by weight)	0.70
Color mixing inhibitor (Cpd-10)	0.05
Solvent (Solv-4)	0.27

Fifth Layer (Red-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM5) sensitized spectrally with red sensitizing dyes (ExS-4, ExS-5)	0.07
Monodisperse silver chlorobromide emulsion (EM6) sensitized spectrally with red sensitizing dyes (ExS-4, ExS-5)	0.16
Gelatin	0.92
Cyan coupler (ExC-1)	0.32
Color image stabilizer (Cpd-8/Cpd-9/Cpd-12 = 3/4/2 by weight)	0.17
Polymeric dispersion medium (Cpd-11)	0.28
Solvent (Solv-2)	0.20

Sixth Layer (Ultraviolet absorbing layer)

Gelatin	0.54
Ultraviolet absorber (Cpd-7/Cpd-9/Cpd-12 = 1/5/3 by weight)	0.21
Solvent (Solv-2)	0.08

Seventh Layer (Protective layer)

Gelatin	1.33
Acryl-modified copolymer of polyvinyl alcohol (modification degree: 17%)	0.17
Liquid paraffin	0.03

Therein, Cpd-13 and Cpd-14 were additionally used as irradiation inhibiting dyes. In each layer, Alkanol XC (produced by du Pont), sodium alkylbenzenesulfonate, a succinic acid ester and Megafac F-120 (produced by Dai-Nippon Ink & Chemicals, Inc.) were further added as coating aids for emulsified dispersions. Furthermore, Cpd-15 and Cpd-16 were used as silver halide stabilizing agent.

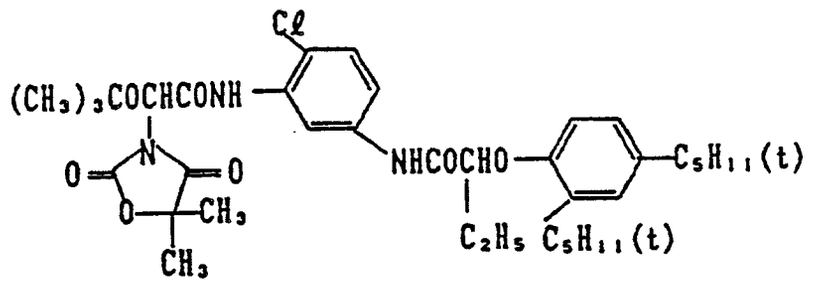
Details of the emulsions used are illustrated below.

Emulsion Name	Crystal Form	Grain Size (μm)	Br Content (mol%)	Variation Coefficient
EM1	Cube	1.0	80	0.08
EM2	Cube	0.75	80	0.07
EM3	Cube	0.5	83	0.09
EM4	Cube	0.4	83	0.10
EM5	Cube	0.5	73	0.09
EM6	Cube	0.4	73	0.10

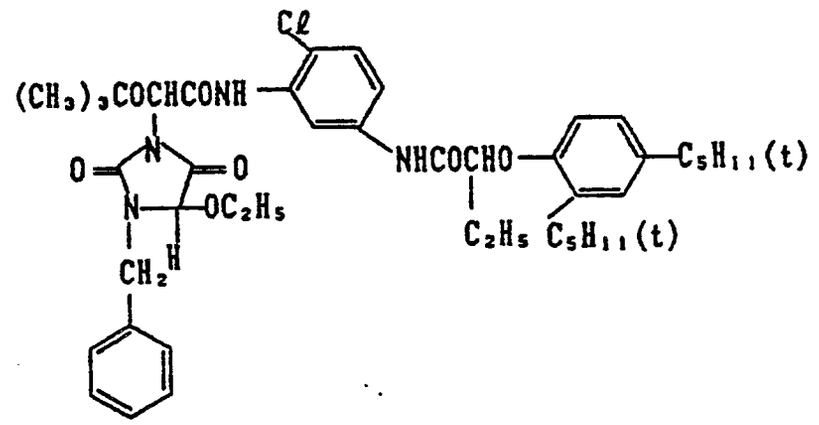
Then, another light-sensitive material was produced in the same manner as described above, except that the compound represented by formula (III) of the present invention was added to the coating composition for the third layer in a proportion of 30 mol% to the magenta coupler.

The structural formulae of the compounds employed are illustrated below.

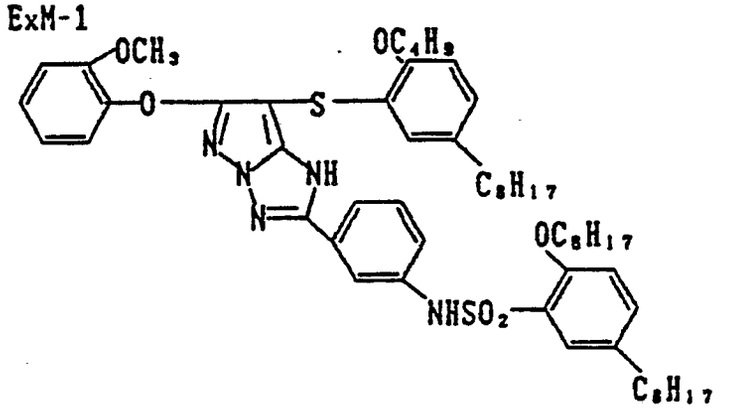
ExY-1



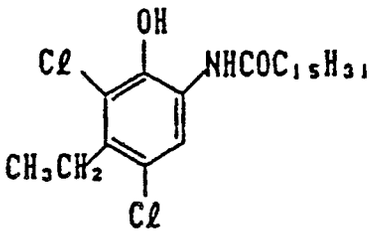
ExY-2



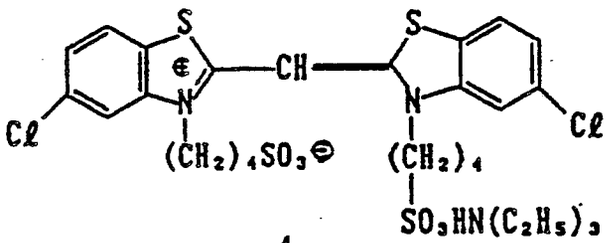
ExM-1



ExC-1

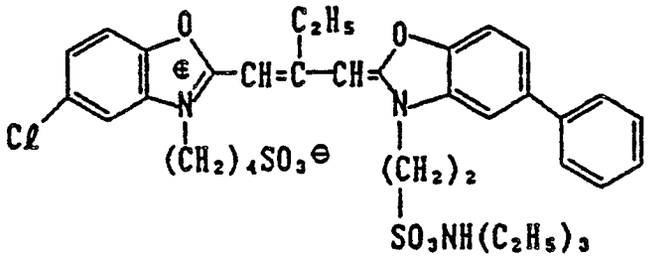


ExS-1



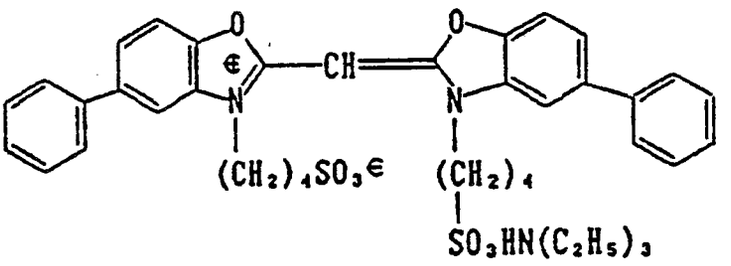
6×10^{-4} mol/mol Ag

ExS-2



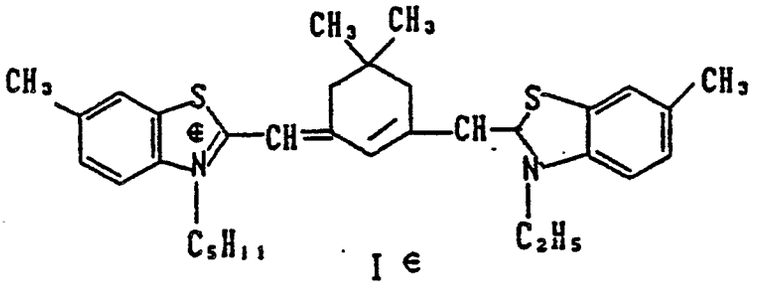
4×10^{-4} mol/mol Ag

ExS-3



8×10^{-4} mol/mol Ag

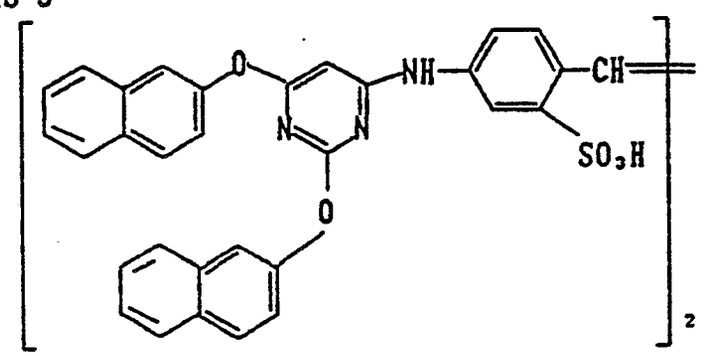
ExS-4



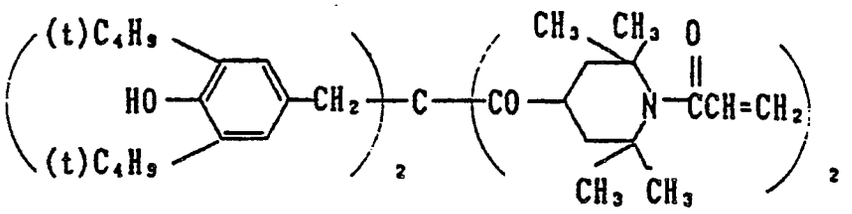
I ⊖

1.8×10^{-4} mol/mol Ag

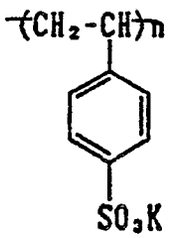
ExS-5



Cpd-1

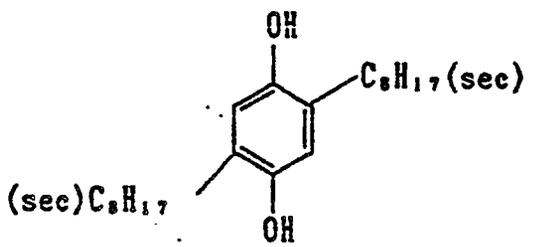


Cpd-2

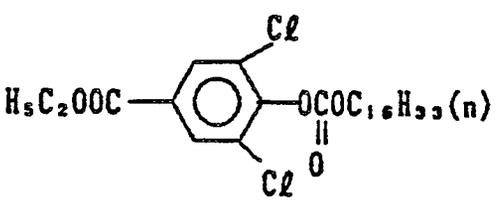


(Molecular Weight:
500,000 - 2,000,000)

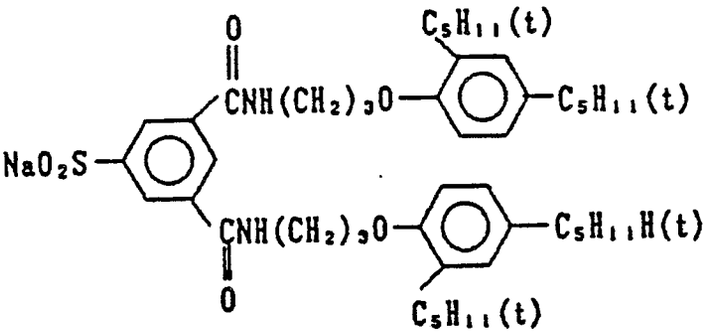
Cpd-3



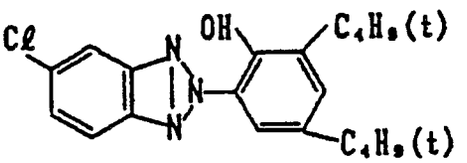
Cpd-5



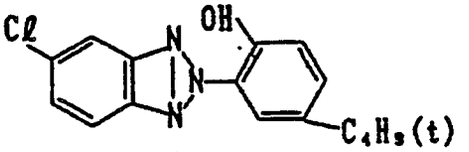
Cpd-6



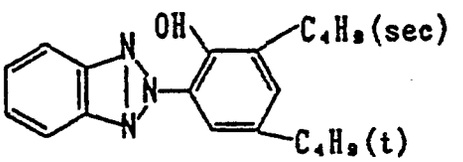
Cpd-7



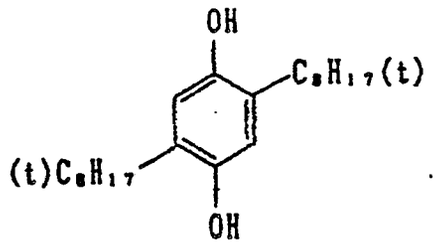
Cpd-8



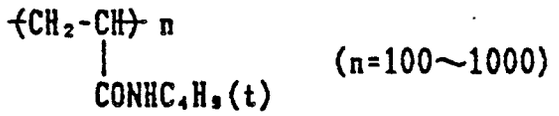
Cpd-9



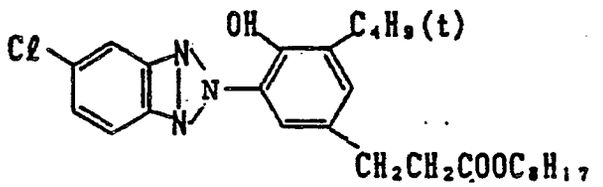
Cpd-10



Cpd-11

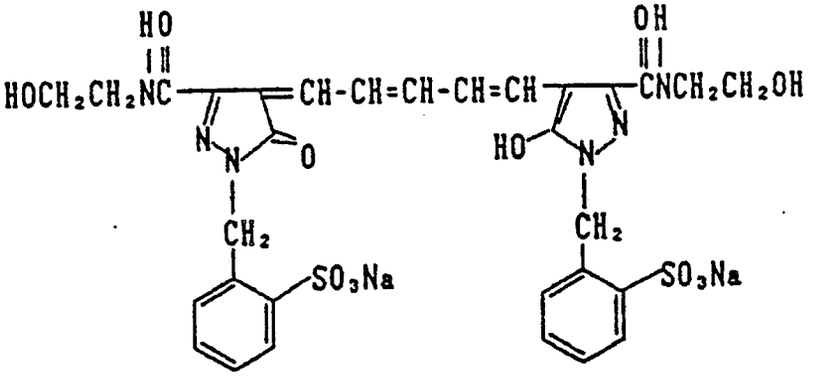


Cpd-12

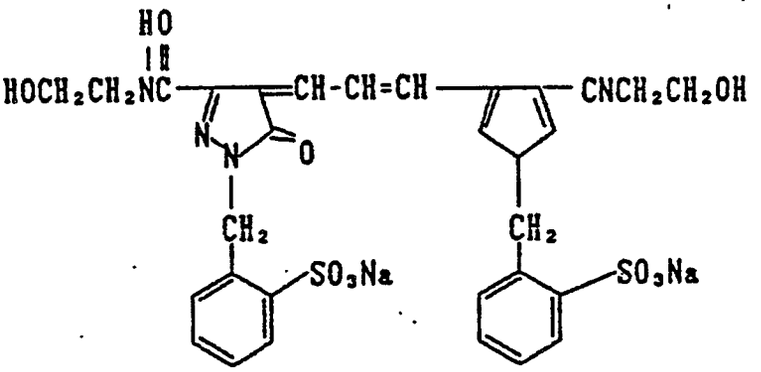


Solv-1 Dibutyl phthalate
Solv-2 Tricresyl phosphate
Solv-3 Trioctyl phosphate
Solv-4 Trinonyl phosphate

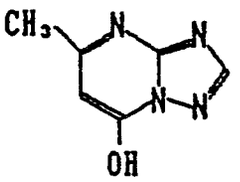
Cpd-13



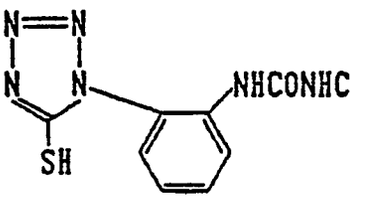
Cpd-14



Cpd-15



Cpd-16



The above-described light-sensitive materials each was exposed to light through an optical wedge, and subjected to photographic processing including the following steps.

Processing Step	Temperature	Time
Color Development	38° C	1 min. 40 sec.
Bleach-Fix	30 to 34° C	1 min. 00 sec.
Rinsing (1)	30 to 34° C	20 sec.
Rinsing (2)	30 to 34° C	20 sec.
Rinsing (3)	30 to 34° C	20 sec.
Drying	70 to 80° C	50 sec.

The rinsing steps were performed in accordance with a countercurrent replenishing process, in which the rinsing bath (3) was replenished with a rinsing solution, and the solution overflowing the rinsing bath (3) was introduced into the rinsing bath (2), and the solution overflowing the rinsing bath (2) was introduced into the rinsing bath (1).

The compositions of the processing solutions used were as follows.

Color Developer:

Water	800 ml
Diethylenetriaminepentaacetic acid	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid (60%)	2.0 g
Nitrilotriacetic acid	2.0 g
Benzyl alcohol	16 ml
Diethylene glycol	10 ml
Sodium sulfite	2.0 g
Potassium bromide	0.5 g
Potassium carbonate	30 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.5 g
Hydroxylamine sulfate	3.0 g
Brightening agent (WHITEX 4B, produced by Sumitomo Chemical Co., Ltd.)	1.5 g
Water to make	1,000 ml
pH (at 25 °C)	10.25

Bleach-fix Bath:

Water	400 ml
Ammonium thiosulfate (70%)	200 ml
Sodium sulfite	20 g
Ammonium ethylenediaminetetraacetatoferrate(III)	60 g
Disodium ethylenediaminetetraacetate	10 g
Water to make	1,000 ml
pH (at 25 °C)	7.00

Rinsing Solution:

Ion exchange water (calcium and magnesium ion concentrations were each below 3 ppm).

Photographic characteristics of these light-sensitive materials were evaluated through measurements of the gradation, the maximum density (D_{max}) and the minimum density (D_{min}). The gradation was expressed in terms of the difference between the density corresponding to the sensitivity point and the density corresponding to the point greater than the sensitivity point by 0.5 in a logarithmic exposure scale. Simultaneously with these measurements, yellow reflection densities in the unexposed areas were measured. Thereafter, the sensitive materials were allowed to stand for 90 days under conditions of 60 °C and 15% RH. Then yellow reflection densities in the unexposed areas were measured again, and thereby the sensitive materials were examined for increments of stains with time after the photographic processing.

The results obtained are shown in Table 1.

TABLE 1

Sensitive Material	Compound	Image Stabilizing Agent	Sulfurous Acid Ion Concentration 0.2 (g/ℓ) D_{min}	0.2 (g/ℓ) D_{max}	0.2 (g/ℓ) Gamma	1.7 (g/ℓ) D_{min}	1.7 (g/ℓ) D_{max}	1.7 (g/ℓ) Gamma	Increment of Stain	Note
A*1)	-	-	0.16	2.71	3.00	0.14	2.50	2.32	+0.13	Comparison
B	-	A-18*2)	0.16	2.73	3.02	0.14	2.69	2.90	+0.21	"
C	III-38	-	0.16	2.72	3.01	0.14	2.68	2.91	+0.11	Invention
D	III-38	A-18*2)	0.15	2.71	2.99	0.14	2.70	2.89	+0.04	"
E	III-35	A-18*2)	0.15	2.73	3.00	0.12	2.68	2.92	+0.05	"
G	III-43	A-18*2)	0.16	2.69	3.00	0.14	2.65	2.92	+0.05	"
H	III-7	A-12*2)	0.18	2.68	2.98	0.18	2.65	2.91	+0.08	"
I	III-23	A-10*2)	0.17	2.69	2.97	0.17	2.65	2.92	+0.08	"
J	III-39	A-16*2)	0.17	2.68	3.00	0.17	2.67	2.91	+0.06	"
K	III-40	A-18*2)	0.14	2.70	2.96	0.13	2.65	2.92	+0.06	"
L	III-39	-	0.16	2.71	2.98	0.13	2.66	2.96	+0.13	"
M	III-39	A-40*3)	0.15	2.71	2.99	0.12	2.67	2.93	+0.10	"
N	III-44	A-51*3)	0.16	2.69	2.97	0.13	2.67	2.91	+0.10	"
O	III-45	A-45*3)	0.16	2.72	2.98	0.12	2.63	2.92	+0.11	"
P	III-47	A-41*3)	0.16	2.71	2.91	0.12	2.67	2.91	+0.10	"

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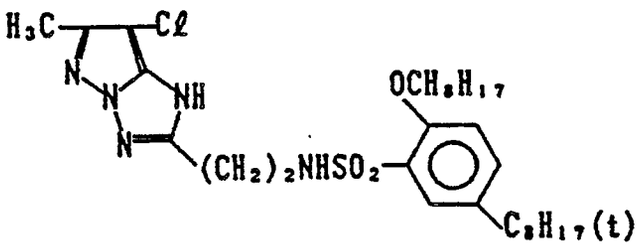
*1) Comparative compound (R-1) having the following formula was added as a magenta coupler to the third layer.

*2) Addition in an equimolar amount to the coupler.

*3) Addition in a proportion of 10 mol% to the coupler.

Comparative Compound (R-1)



As can be seen from the data in Table 1, not only the processing results obtained using the light-sensitive materials of the present invention showed a considerably reduced dependence on the sulfurous acid ion concentration, but also an increase of stain with time after the processing was remarkably depressed in the light-sensitive materials of the present invention. This depression effect on the generation of stain with time after the processing was more remarkable with the addition of the present compound of formula (III) than the image stabilizing agent of formula (IV) or (V).

EXAMPLE 2

On a paper support laminated with a polyethylene film on both sides thereof, were coated the layers described below in this order to prepare a multilayer silver halide light-sensitive material. Coating compositions were prepared in the following manner.

Preparation of Coating Composition for First Layer:

To 19.1 g of a yellow coupler (ExY-1) and 4.4 g of a color image stabilizer (Cpd-1), were added 27.2 ml of ethyl acetate and 7.7 ml (8.0 g) of a high boiling solvent (Solv-1) to make a solution. The solution was emulsified and dispersed in 185 ml of a 10% aqueous gelatin solution containing 8 ml of a 10% sodium dodecylbenzenesulfonate solution. The resulting emulsified dispersion was mixed homogeneously with the emulsions EM7 and EM8, and further the gelatin concentration therein was adjusted so that the resulting emulsion had the composition described below. Thus, the coating composition for the first layer was prepared.

Coating compositions for the second to the seventh layers were prepared in the same manner as for the first layer. In each layer, sodium salt of 1-hydroxy-3,5-dichloro-s-triazine was contained as gelatin hardener. In addition, Cpd-2 was used as viscosity increasing agent.

Constituent Layers:

The ingredients used and their coverages expressed in terms of g/m^2 are described below, with the coverage of silver halide expressed on a silver basis.

Support

Polyethylene-laminated paper (containing a white pigment (TiO_2) and a bluish dye on the first layer side).

First Layer (Blue-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM7) sensitized spectrally with a blue sensitizing dye (ExS-1)	0.15
Monodisperse silver chlorobromide emulsion (EM8) sensitized spectrally with a blue sensitizing dye (ExS-1)	0.15
Gelatin	1.86
Yellow coupler (ExY-1)	0.82
Color image stabilizer (Cpd-1)	0.19
Solvent (Solv-1)	0.35

Second Layer (Color mixing inhibiting layer)

Gelatin	0.99
Color mixing inhibitor (Cpd-3)	0.08

Third Layer (Green-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM9) sensitized spectrally with green sensitizing dyes (ExS-2, ExS-3)	0.12
Monodisperse silver chlorobromide emulsion (EM10) sensitized spectrally with green sensitizing dyes (ExS-2, ExS-3)	0.24
Gelatin	1.24
Magenta coupler (ExM-1)	0.39
Color image stabilizer (Cpd-4)	0.25
Color image stabilizer (Cpd-5)	0.12
Solvent (Solv-2)	0.25

Fourth Layer (Ultraviolet absorbing layer)

Gelatin	1.60
Ultraviolet absorber (Cpd-6/Cpd-7/Cpd-8 = 3/2/6 by weight)	0.70
Color mixing inhibitor (Cpd-9)	0.05
Solvent (Solv-3)	0.42

Fifth Layer (Red-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM11) sensitized spectrally with red sensitizing dyes (ExS-4, ExS-5)	0.07
Monodisperse silver chlorobromide emulsion (EM12) sensitized spectrally with red sensitizing dyes (ExS-4, ExS-5)	0.16
Gelatin	0.92
Cyan coupler (ExC-1)	0.15
Cyan coupler (ExC-2)	0.18
Color image stabilizer (Cpd-7/Cpd-8/Cpd-10 = 3/4/2 by weight)	0.17
Polymeric dispersion medium (Cpd-11)	0.14
Solvent (Solv-1)	0.20

Sixth Layer (Ultraviolet absorbing layer)

Gelatin	0.54
Ultraviolet absorber (Cpd-6/Cpd-8/Cpd-12 = 1/5/3 by weight)	0.21
Solvent (Solv-4)	0.08

Seventh Layer (Protective layer)

Gelatin	1.33
Acrylmodified copolymer of polyvinyl alcohol (modification degree: 17%)	0.17
Liquid paraffin	0.03

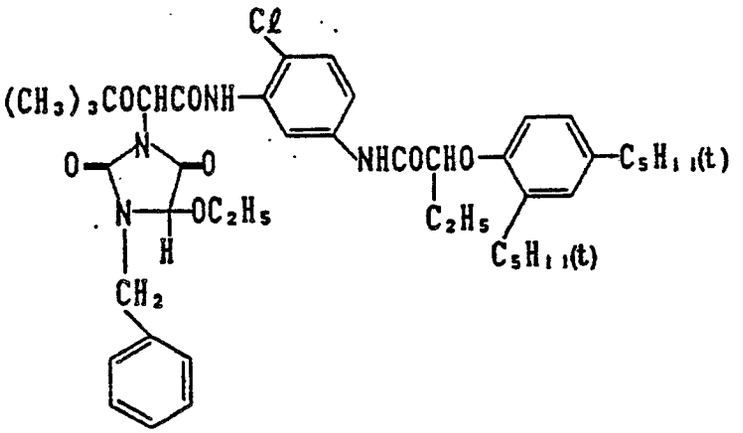
Therein, Cpd-12 and Cpd-13 were additionally used as irradiation inhibiting dyes. In each layer, Alkanol XC (produced by du Pont), sodium alkylbenzenesulfonate, a succinic acid ester and Megafac F-120 (produced by Dai-Nippon Ink & Chemicals, Inc.) were further added as coating aids for emulsified dispersions. Furthermore, Cpd-14 and Cpd-15 were used as silver halide stabilizing agent.

Details of the emulsions used are illustrated below.

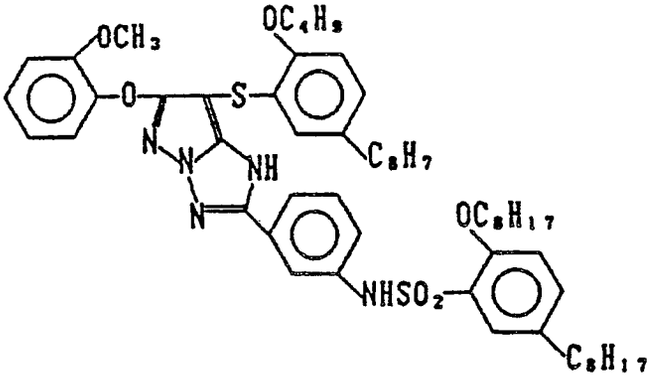
Emulsion Name	Crystal Form	Grain Size (μm)	Br Content (mol%)	Variation Coefficient
EM7	Cube	1.1	1.0	0.10
EM8	Cube	0.8	1.0	0.10
EM9	Cube	0.45	1.5	0.09
EM10	Cube	0.34	1.5	0.09
EM11	Cube	0.45	1.5	0.09
EM12	Cube	0.34	1.6	0.10
(Variation Coefficient = Standard Deviation/Average Size)				

The structural formulae of the compounds employed are illustrated below.

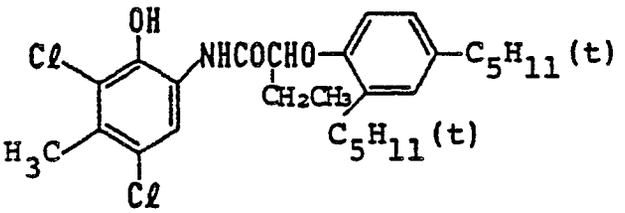
ExY-1



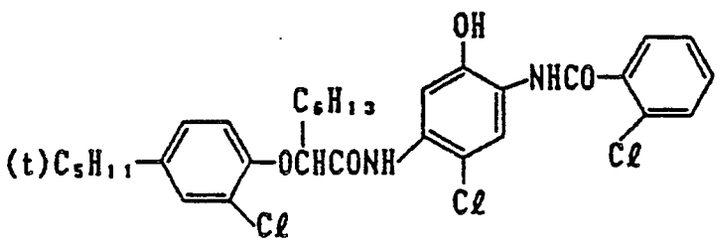
ExM-1



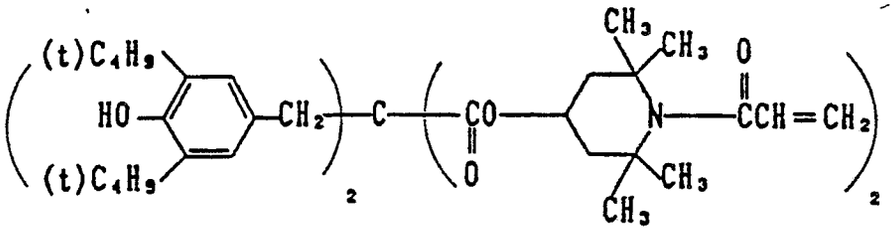
ExC-1



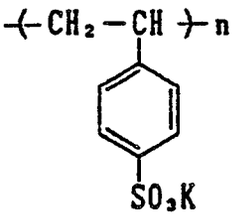
ExC-2



Cpd-1

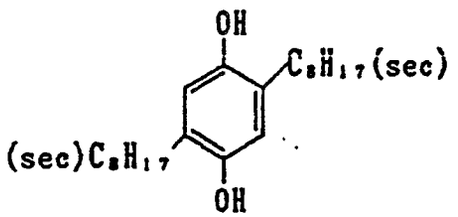


Cpd-2

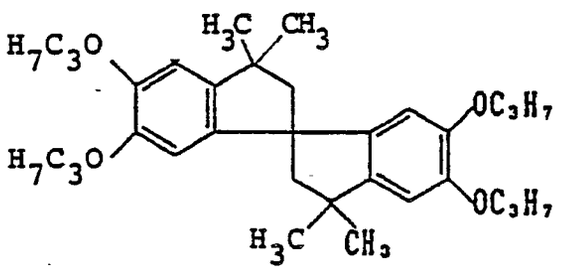


(Molecular Weight: 500,000-2,000,000)

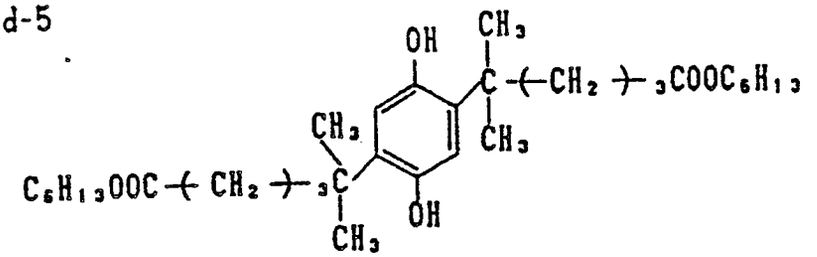
Cpd-3



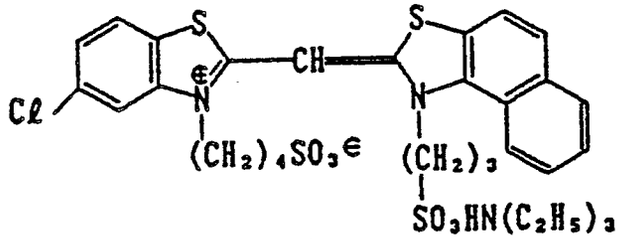
Cpd-4



Cpd-5

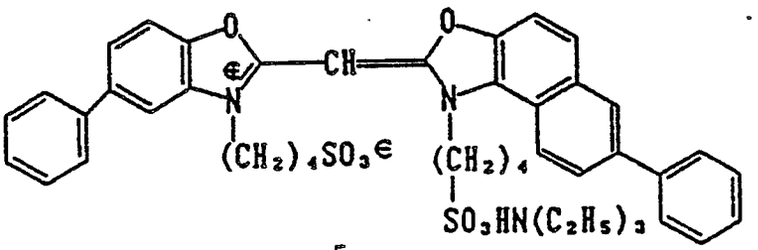


ExS-1



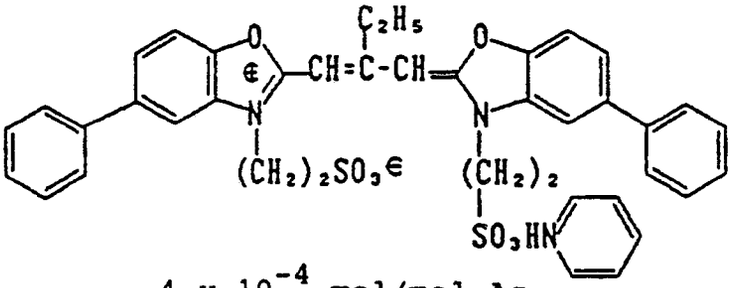
6×10^{-4} mol/mol Ag

ExS-2



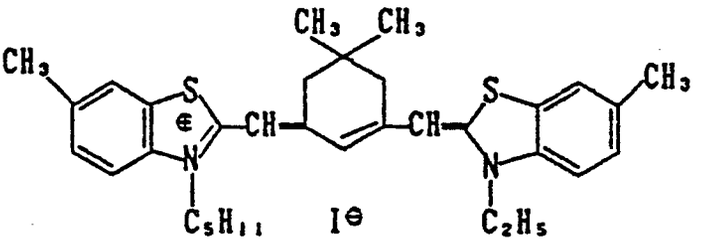
8×10^{-5} mol/mol Ag

ExS-3



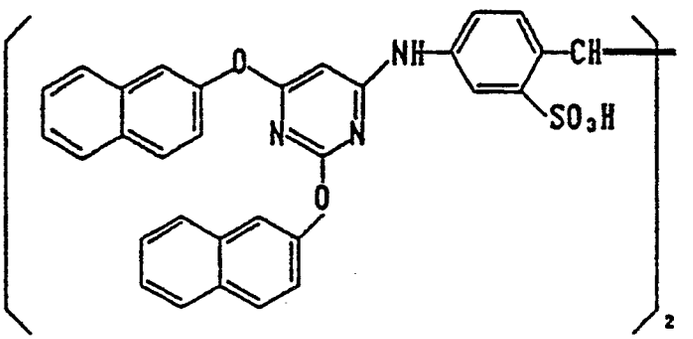
4 x 10^{-4} mol/mol Ag

ExS-4

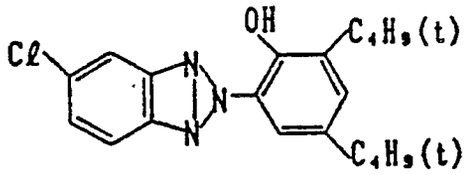


1.8 x 10^{-4} mol/mol Ag

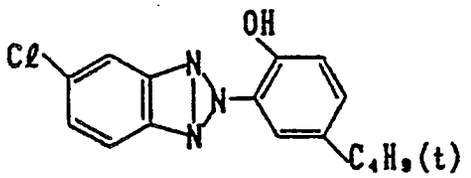
ExS-5



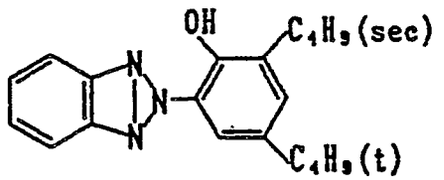
Cpd-6



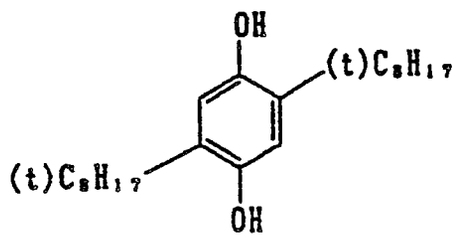
Cpd-7



Cpd-8



Cpd-9



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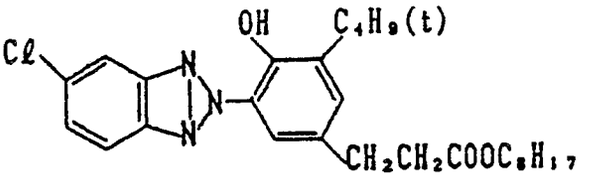
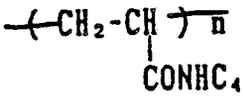


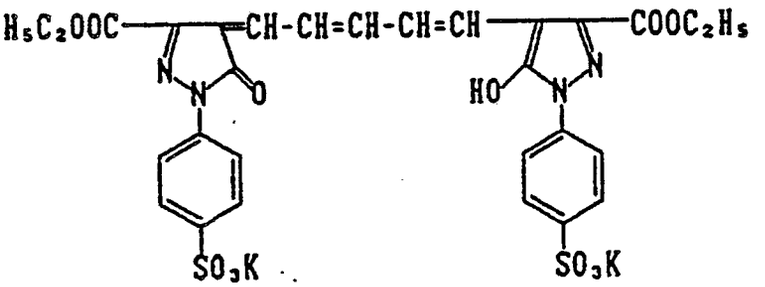
Cpd-11



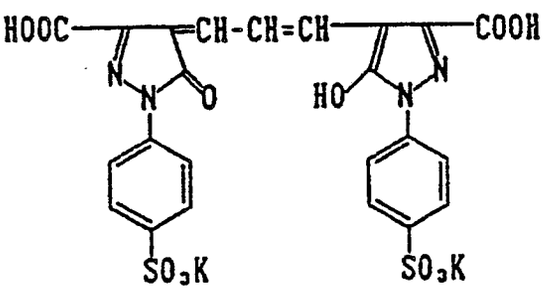
(n=100~1000)

Molecular weight: 100,000

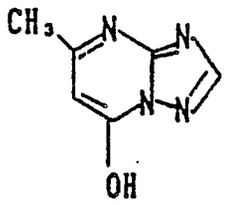
Cpd-12



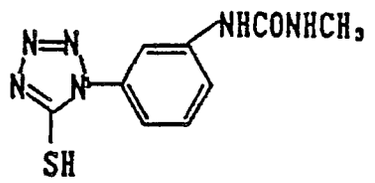
Cpd-13



Cpd-14



Cpd-15



Solv-1 Dibutyl Phthalate
Solv-2 Trioctyl Phosphate
Solv-3 Trinonyl Phosphate
Solv-4 Tricresyl Phosphate

The foregoing light-sensitive material was imagewise exposed, and then subjected to a running processing test with a paper processing machine which included the following steps. The running processing test was contained till the color developer was replenished in twice as much amount as the tank volume.

Processing Step	Temperature (°C)	Time (sec.)	Amount Replenished*(-ml)	Tank Volume (ℓ)
Color development	38	45	161	17
Bleach-Fix	30 to 36	45	161	17
Rinsing (1)	30 to 37	20	-	10
Rinsing (2)	30 to 37	20	-	10
Rinsing (3)	30 to 37	20	-	10
Rinsing (4)	30 to 37	30	248	10
Drying	75 to 80	60		

* per 1 m^2 of the light-sensitive material processed.

The replenishment of the rinsing solution was performed in the direction from the rinsing tank (4) to the rinsing tank (1) according to a four-tank counter replenishing process.

The compositions of the processing solutions used were as follows.

Color Developer

	Tank Solution	Replenisher
Water	800 ml	800 ml
Ethylenediamine-N,N,N,N-tetramethylenephosphonic acid	1.5 g	1.5 g
Triethylenediamine(1,4-diazabicyclo[2,2,2]octane)	5.0 g	5.0 g
Sodium chloride	1.4 g	
Potassium carbonate	25 g	25 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g	7.0 g
Diethylhydroxylamine	4.2 g	6.0 g
Brightening agent (4,4'-diaminostilbene type)	2.0 g	2.5 g
Water to make	1,000 ml	1,000 ml
pH (at 25° C)	10.05	10.45

Bleach-fix Bath (Tank solution = Replenisher)

Water	400 ml
Ammonium thiosulfate (70%)	100 ml
Sodium sulfite	17 g
Ammonium ethylenediaminetetraacetatoferrate(III)	55 g
Disodium ethylenediaminetetraacetate dihydrate	5 g
Ammonium bromide	40 g
Glacial acetic acid	9 g
Water to make	1,000 ml
pH (at 25° C)	5.40

Rinsing Solution (Tank solution = Replenisher)

Ion-exchanged water (in which calcium and magnesium ion concentrations were each below 3 ppm).

In addition, light-sensitive materials were prepared in the same manner as for the foregoing material, except that the magenta couplers set forth in Table 2 were employed as the magenta coupler in the third layer, respectively, and the compounds represented by the general formula (III) of the present invention were further added in a proportion of 30 mol% to the couplers, respectively.

Photographic characteristics and an increase of stain with time after the processing were examined by the same methods as in Example 1.

The results are shown in Table 2.

TABLE 2

Sensitive Material	Coupler in Third Layer	Compound of Invention	Photographic Characteristics						Increment of Stain	Note
			Fresh Developer			Running developer				
			D_{min}	D_{max}	Gamma	D_{min}	D_{max}	Gamma		
II-A	R-1*1)	-	0.12	2.10	2.51	0.18	1.86	2.10	+0.12	Comparison
II-B	R-1*1)	III-38	0.12	1.96	2.50	0.17	1.77	2.09	+0.12	"
II-C	M-6	-	0.12	2.88	2.99	0.13	2.89	2.91	+0.26	"
II-D	M-6	III-38	0.12	2.89	3.00	0.13	2.88	3.02	+0.11	Invention
II-E	M-10	III-38	0.12	2.79	2.96	0.13	2.77	2.98	+0.09	"
II-F	M-52	III-38	0.11	2.82	3.01	0.13	2.80	2.99	+0.10	"
II-G	M-54	III-38	0.12	2.61	2.82	0.14	2.59	2.80	+0.11	"
II-H	M-34	III-38	0.12	2.62	2.81	0.13	2.56	2.77	+0.11	"
II-I	M-40	III-38	0.13	2.61	2.80	0.13	2.56	2.78	+0.11	"
II-J	M-56	III-39	0.13	2.90	3.02	0.14	2.86	3.00	+0.08	"
II-K	M-60	III-39	0.12	2.89	2.98	0.13	2.87	2.96	+0.07	"
II-L	M-62	III-39	0.12	2.88	3.00	0.12	2.84	2.96	+0.08	"
II-M	M-70	III-39	0.12	2.61	2.81	0.12	2.56	2.77	+0.09	"
II-N	M-71	III-39	0.13	2.60	2.80	0.13	2.54	2.76	+0.09	"

*1) R-1 was the same as in Example 1.

As can be seen from Table 2, the light-sensitive materials of the present invention showed not only slight changes of photographic characteristics by running processing, but also a considerably depressed increase in stain density with time after the processing.

EXAMPLE 3

On a paper laminated with polyethylene on both sides and subjected to a corona discharge treatment, the layers of from the first layer (the lowest layer) to the seventh layer (the uppermost layer) were coated in this order to prepare a light-sensitive material. Coating compositions for these layers were prepared in the manner described below. The structural formulae and other details of the couplers, the color image stabilizers and other ingredients used therein are described below.

A coating composition for the first layer was prepared as follows: A mixture of 200 g of a yellow coupler, 93.3 g of a discoloration inhibitor, 10 g of a high boiling point solvent (p), 5 g of a solvent (g) was added to 600 ml of ethyl acetate as an auxiliary solvent, and dissolved therein by heating to 60 °C. The resulting solution was mixed with 3,300 ml of a 5% aqueous gelatin solution containing 330 ml of a 5% aqueous solution of Alkanol B (trade name of alkylnaphthalenesulfonate produced by du Pont), and emulsified with a colloid mill to prepare a color dispersion. The ethyl acetate was distilled away from the color dispersion under reduced pressure. The resulting dispersion was added to 1,400 g of an emulsion (containing 96.7 g of silver and 170 g of gelatin) to which a sensitizing dye for a blue-sensitive emulsion layer and 1-methyl-2-mercapto-5-acetylamino-1,3,4-triazole had been added, and thereto was further added 2,600 g of a 10% aqueous gelatin solution. Thus, the coating composition was prepared.

Constituent Layers

The ingredients used and their coverages expressed in terms of mg/m^2 are described below, with the coverage of silver halide expressed on a silver basis.

Support:

Paper support laminated by polyethylene on both sides.

First Layer (Blue-sensitive Layer):

Silver chlorobromide emulsion (bromide content: 80 mol%)	290
Yellow coupler	600
Discoloration inhibitor (r)	280
Solvent (p)	30
Solvent (q)	15
Gelatin	1800

Second Layer (Color Mixing Inhibiting Layer):

Silver bromide emulsion (primitive, 0.05 μm grain size)	Silver 10
Color mixing inhibitor (s)	55
Solvent (p)	30
Solvent (q)	15
Gelatin	800

Third Layer (Green-sensitive Layer):

Silver chlorobromide emulsion (bromide content: 70 mol%)	305
Magenta coupler	670
Discoloration inhibitor (t)	150
Compound of invention (III-38)	30
Discolorationn inhibitor (u)	10
Solvent (p)	200
Solvent (g)	10
Gelatin	1400

Fourth Layer (Color Mixing Inhibiting Layer):

Color mixing inhibitor (s)	65
Ultraviolet absorber (n)	450
Ultraviolet absorber (o)	230
Solvent (p)	50
Solvent (q)	50
Gelatin	1700

Fifth Layer (Red-sensitive Layer):

Silver chlorobromide emulsion (bromide content: 70 mol%)	210
Cyan coupler	380
Discoloration inhibitor (r)	250
Solvent (p)	160
Solvent (q)	100
Gelatin	1800

Sixth Layer (Ultraviolet Absorbing Layer):

Ultraviolet absorber (n)	260
Ultraviolet absorber (o)	70
Solvent (p)	300
Solvent (q)	100
Gelatin	700

Seventh Layer (Protective Layer):

Gelatin	620
n: 2-(2-Hydroxy--3,5-di-tert-amylphenyl)benzotriazole	
o: 2-(2-Hydroxy--3,5-di-tert-butylphenyl)benzotriazole	
p: Di(2-ethylhexyl)phthalate	
q: Dibutyl phthalate	
r: 2,5-Di-tert-amylphenyl-3,5--di-tert-butylhydroxybenzoate	
s: 2,5-Di-tert-octylhydroquinone	
t: 1,4-Di-tert-amyl-2,5-dioctyloxybenzene	

The following compounds were used as sensitizing dye for each emulsion layer.

Blue-sensitive emulsion layer:

Anhydro-5-methoxy-5′-methyl-3,3-disulfopropylselenacyanine hydroxide

Green sensitive emulsion layer:

Anhydro-9-ethyl-5,5′-di-phenyl-3,3′-disulfoethyloxacarbocyanine hydroxide

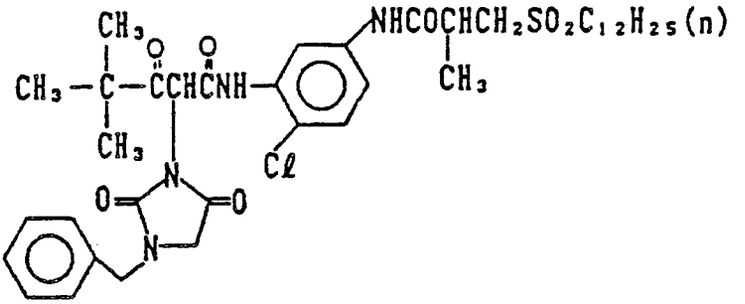
Red-sensitive emulsion layer:

3,3′-Diethyl-5 methoxy-9,9′-(2,2-dimethyl-1,3-propano)thiadicarbocyanine iodide

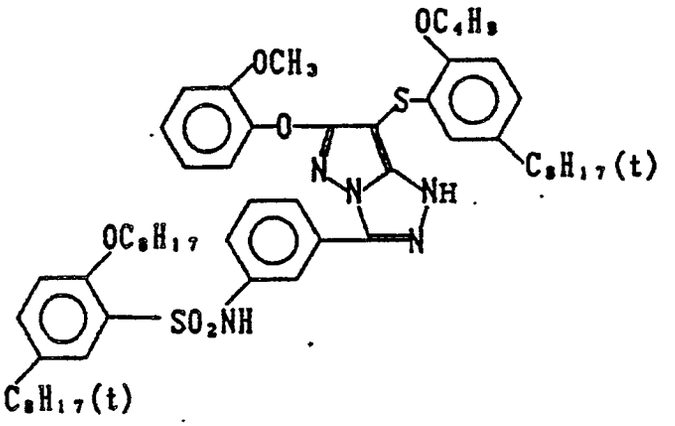
In addition, 1-methyl-2 mercapto-5-acetylamino-1,3,4-triazole was used as a stabilizer for each layer. Further, dipotassium 4-(3-carboxy-5-hydroxy-4-(3-carboxy-5-oxo-1-(4-sulfonatophenyl)-pyrazoline-4-ylidene)-1-propenyl)-1-pyrazolyl)benzenesulfonate, and tetrasodium N,N′-(4,8-dihydroxy-9,10-di-oxo-3,7-disulfonatoanthracene-1,5-diyl)bis(aminomethanesulfonate) were used as irradiation preventing dyes. Furthermore, 1,2-bis(vinylsulfonyl)ethane was used as hardener.

The couplers used and the discoloration inhibitor (u) used are illustrated below.

Yellow Coupler

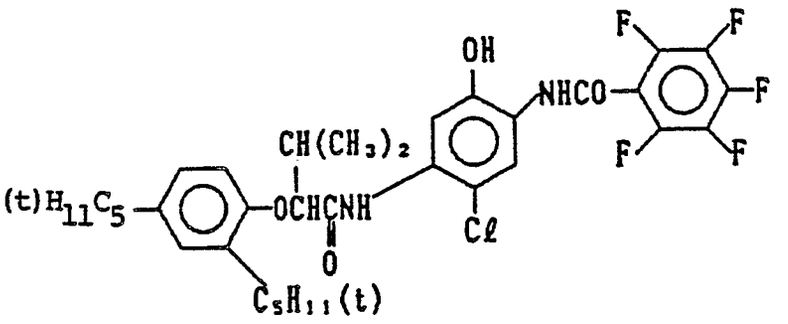


Magenta Coupler

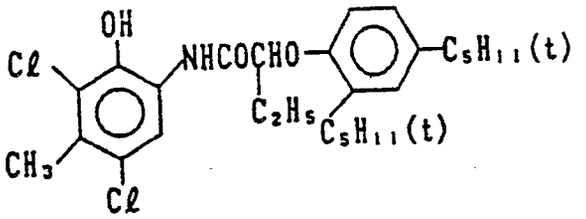


Cyan Coupler

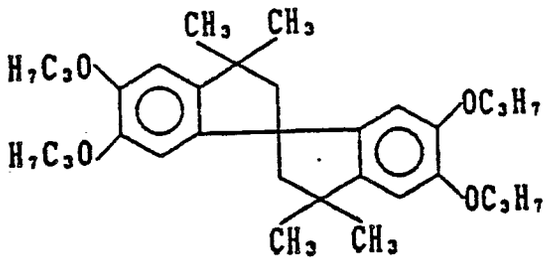
Equimolar amount of



and



Discoloration Inhibitor (u)



After the processing, the photographic characteristics were evaluated by the same procedures as in Example 1, and the same results as in Example 1 were obtained.

EXAMPLE 4

The following layers from the first to the eleventh were coated on a paper support laminated by polyethylene on both sides thereof to prepare a light-sensitive material. The polyethylene laminated on the first layer side contained titanium white as a white pigment and a trace amount of ultramarine blue as a bluish dye.

The ingredients used and their coverages expressed in terms of g/m^2 are described below, with the coverage of silver halide represented on a silver basis.

Constituent Layers

First Layer (Antihalation Layer):

Black colloidal silver	0.10
Gelatin	2.00

Second Layer (Slow Red-sensitive Layer):

Silver iodobromide (having an iodide content of 3.5 mol%, and an average grain size of 0.5 μm) sensitized spectrally with red sensitizing dyes (ExS-1 and ExS-2)	0.15
Gelatin	1.00
Cyan coupler (ExC-1)	0.30
Discoloration inhibitor (Cpd-1, Cpd-2 and Cpd-3, 4:4:2 by weight)	0.15
Coupler solvent (Solv-1 and Solv-2, 1:1 by weight)	0.06

Third Layer (High-speed Red-sensitive Layer):

Silver iodobromide (having an iodide content of 8.0 mol%, and an average grain size of 0.60 μm) sensitized spectrally with red sensitizing dyes (ExS-1 and ExS-2)	0.11
Gelatin	0.50
Cyan coupler (ExC-1)	0.10
Discoloration inhibitor (Cpd-1, Cpd-2 and Cpd-3, 4:4:2 by weight))	0.05
Coupler solvent (Solv-1 and Solv-2, 1:1 by weight)	0.04

Fourth Layer (Interlayer):

Yellow colloidal silver	0.02
Gelatin	1.00
Color mixing inhibitor (Cpd-4)	0.08
Color mixing inhibitor solvent (Solv-3 and Solv-4, 1:1 by weight)	0.16
Polymer latex (Cpd-5)	0.10

Fifth Layer (Slow Green-sensitive Layer):

Silver iodobromide (having an iodide content of 2.5 mol%, and an average grain size of 0.4 μm) sensitized spectrally with green sensitizing dye (ExS-3)	0.20
Gelatin	0.70
Magenta coupler (ExM-1)	0.40
Discoloration inhibitor (Cpd-6)	0.05
Discoloration inhibitor (Cpd-7)	0.05
Discoloration inhibitor (Cpd-8)	0.02
Compound of invention (III-38)	0.06
Coupler solvent (Solv-3 and Solv-5, 1:1 by weight)	0.15

Sixth Layer (High-speed Green-sensitive Layer):

Silver iodobromide (having an iodide content of 3.5 mol%, and an average grain size of 0.9 μm) sensitized spectrally with green sensitizing dye (ExS-3)	0.20
Gelatin	0.70
Magenta coupler (ExM-1)	0.40
Discoloration inhibitor (Cpd-6)	0.05
Discoloration inhibitor (Cpd-7)	0.05
Discoloration inhibitor (Cpd-8)	0.02
Compound of invention (III-38)	0.06
Coupler solvent (Solv-3 and Solv-5, 1:1 by weight)	0.15

Seventh Layer (Yellow Filter Layer):

Yellow colloidal silver	0.20
Gelatin	1.00
Color mixing inhibitor (Cpd-4)	0.06
Color mixing inhibitor solvent (Solv-3 and Solv-5, 1:1 by weight)	0.15
Polymer latex (Cpd-8)	0.10

Eighth Layer (Slow Blue-sensitive Layer):

Silver iodobromide (having an iodide content of 2.5 mol%, and an average grain size of 0.5 μm) sensitized spectrally with blue sensitizing dye (ExS-4)	0.15
Gelatin	0.50
Yellow coupler (ExY-1)	0.20
Stain inhibitor (Cpd-8)	0.001
Coupler solvent (Solv-2)	0.05

Ninth Layer (High-speed Blue-sensitive Layer):

Silver iodobromide (having an iodide content of 2.5 mol%, and an average grain size of 1.4 μm) sensitized spectrally with green sensitizing dye (ExS-4)	0.20
Gelatin	0.50
Yellow coupler (ExY-1)	0.20
Stain inhibitor (Cpd-8)	0.001
Coupler solvent (Solv-2)	0.05

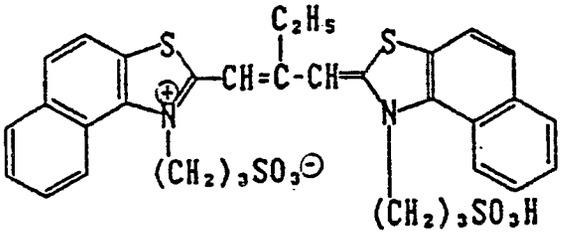
Tenth Layer (Ultraviolet Absorbing Layer):

Gelatin	1.50
Ultraviolet absorber (Cpd-9, Cpd-1 and Cpd-3, 4:4:2 by weight)	1.00
Color mixing inhibitor (Cpd-10)	0.08
Ultraviolet absorber solvent (Solv-2)	0.30
Irradiation preventing dye (Cpd-11)	0.04
Irradiation preventing dye (Cpd-12)	0.04

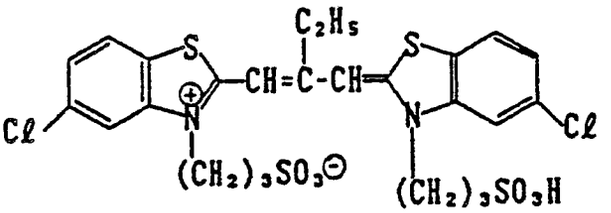
Eleventh Layer (Protective Layer):

Fine-grained silver chlorobromide (having a chloride content of 97 mol% and an average grain size of 0.2 μm)	0.07
Gelatin	1.00
Gelatin hardener (H-1)	0.17

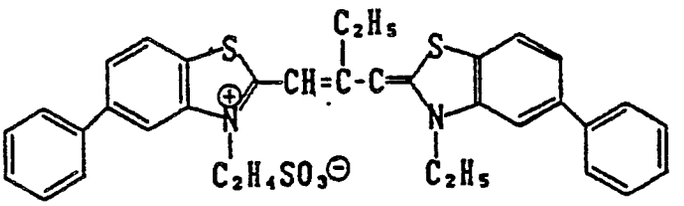
ExS-1



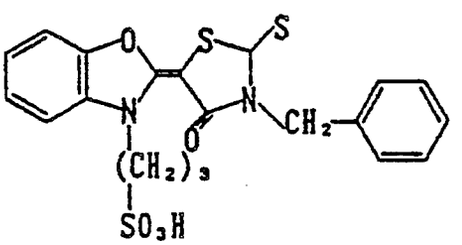
ExS-2



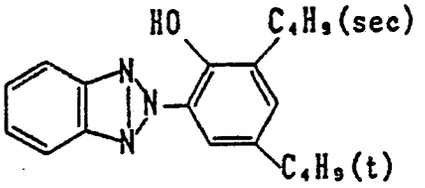
ExS-3



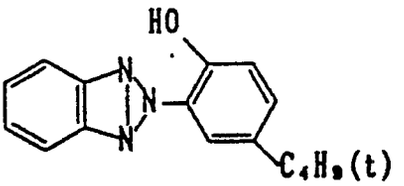
ExS-4



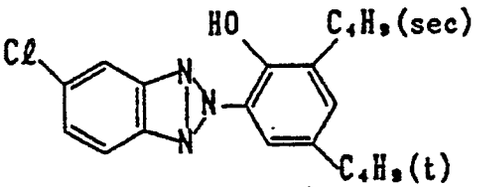
Cpd-1



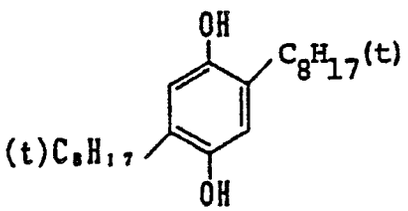
Cpd-2



Cpd-3



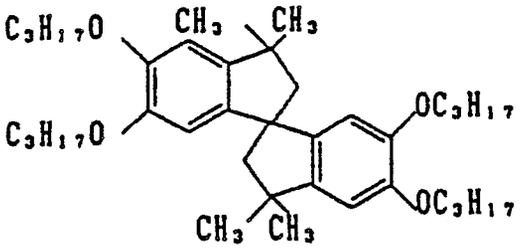
Cpd-4



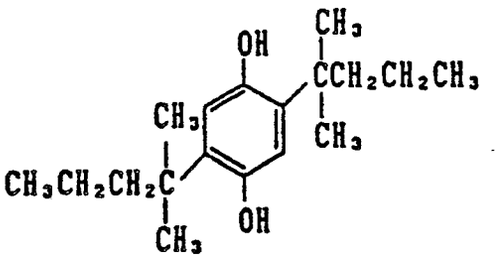
Cpd-5

Polyethyl acrylate

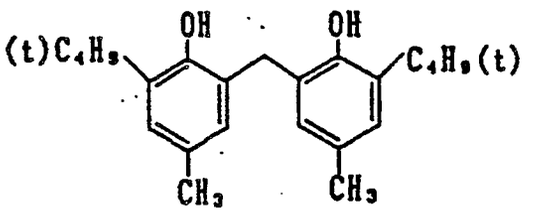
Cpd-6



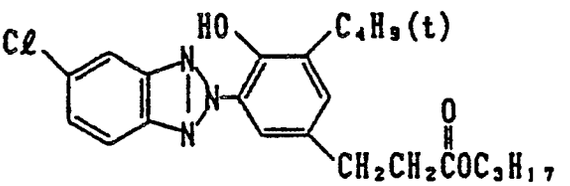
Cpd-7



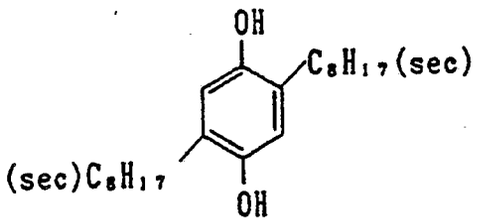
Cpd-8



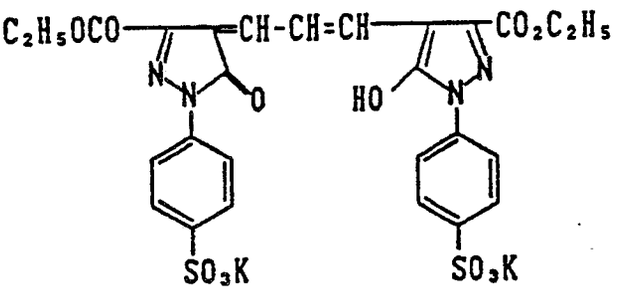
Cpd-9



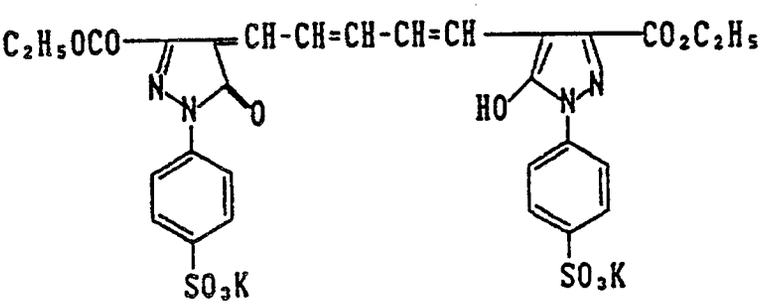
Cpd-10



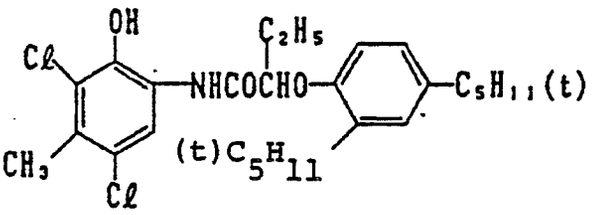
Cpd-11



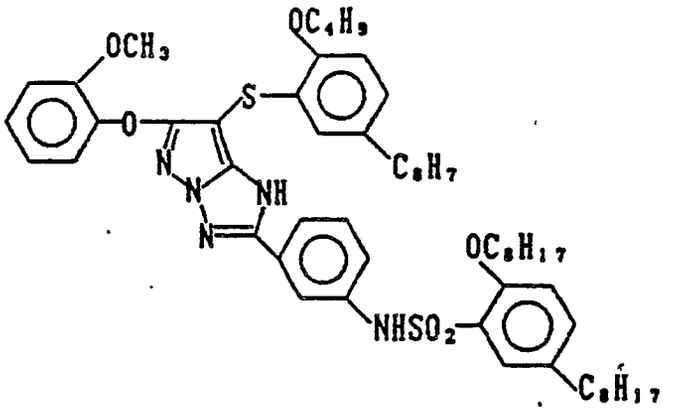
Cpd-12



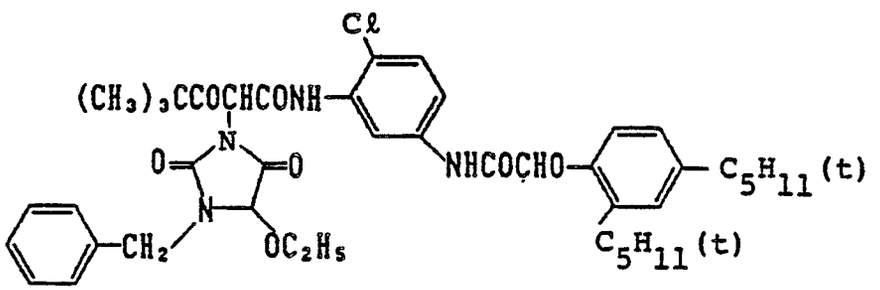
ExC-1



ExM-1



ExY-1



Solv-1
Di(2-ethylhexyl)phthalate
Solv-2
Trinonyl phosphate
Solv-3
Tricresyl phosphate
Solv-4
Dibutyl phthalate
Solv-5
Trioctyl phosphate
H-1
1,2-Bis(vinylsulfonylacetamido)ethane

The thus prepared silver halide color photographic material was exposed to light, and then processed with an automatic developing machine in which the following steps were continued until total replenished amount of each processing solution became three times the corresponding tank volume. The results obtained were similar to those obtained in Example 1.

Processing Steps	Time	Temperature	Tank Solution	Amount replenished
First development	75 sec.	38°C	8 ℓ	330 ml/m²
First Water Washing (1)	45 sec.	33°C	5 ℓ	-
First Water Washing (2)	45 sec.	33°C	5 ℓ	5000 ml/m²
Reversal Exposure	15 sec.	100 lux.		
Color Development	135 sec.	38°C	15 ℓ	330 ml/m²
Second Water Washing	45 sec.	33°C	5 ℓ	1000 ml/m²
Bleach-Fix (1)	60 sec.	38°C	7 ℓ	-
Bleach-Fix (2)	60 sec.	38°C	7 ℓ	220 ml/m²
Third Water Washing (1)	45 sec.	33°C	5 ℓ	-
Third Water Washing (2)	45 sec.	33°C	5 ℓ	-
Third Water Washing (3)	45 sec.	33°C	5 ℓ	5000 ml/m²
Drying	45 sec.	75°C		

The replenishment in the first and the third water washing steps was performed in accordance with acountercurrent replenishing process, wherein the washing bath of the first water washing (2) was supplied with washing water, the overflowing solution therefrom introduced into the washing bath of the first water washing (1), the washing bath of the third water washing (3) was supplied with washingwater, teh overflowing solution therefrom was introduced into the washing bath of the third water washing(2), and the overflowing solution therefrom was introduced into the washing bath of the third water washing (1).

The compositions of the processing solutions used were as follows.

First Developer

	Tank Solution	Replenisher
Pentasodium nitrilo-N,N,N-trimethylenephosphonate	1.0 g	1.0 g
Pentasodium diethylenetriaminepentaacetate	3.0 g	3.0 g
Potassium sulfite	30.0 g	30.0 g
Potassium thiocyanate	1.2 g	1.2 g
Potasssium carbonate	35.0 g	35.0 g
Potassium hydroquinonemonosulfonate	25.0 g	25.0 g
1-Phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidone	2.0 g	2.0 g
Potassium bromide	0.5 g	-
Potassium iodide	5.0 mg	-
Water to make	1000 ml	1000 ml
pH	9.60	9.70

PH was adjusted with hydrochloric acid or potassium hydroxide.

Color Developer

	Tank Solution	Replenisher
Benzyl alcohol	15.0 ml	18.0 ml
Diethylene glycol	12.0 ml	14.0 ml
3,6-Dithia-1,8-octanediol	0.20 g	0.25 g
Pentasodium nitrilo-N,N,N-trimethylenephosphonate	0.5 g	0.5 g
Pentasodium diethylenetriaminepentaacetate	2.0 g	2.0 g
Sodium sulfite	2.0 g	2.5 g
Hydroxylamine sulfate	3.0 g	3.6 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g	8.0 g

EXAMPLE 5

A multilayer color photosensitive material having the layer structure shown below on a paper support laminated with polyethylene on both sides thereof was prepared.

E9 Layer	Protective layer
E8 Layer	Ultraviolet absorbing layer
E7 Layer	Blue-sensitive emulsion layer
E6 Layer	Interlayer
E5 Layer	Yellow filter layer
E4 Layer	Interlayer
E3 Layer	Green-sensitive emulsion layer
E2 Layer	Interlayer
E1 Layer	Red-sensitive emulsion layer
Support	
B1 Layer	Backing layer
B2 Layer	Protective layer

Compositions of these layers are described below. The coverages are expressed in g/m^2, and the coverages of silver halide emulsions and colloidal silvers are those based on silver. The amounts of spectral sensitizing dyes are addition amounts expressed in mol per mol of silver halide in the same layer.

Support

Polyethylene-laminated paper (the polyethylene laminate on the E1 layer side contained a white pigment (TiO_2) and a bluish dye (ultramarine)).

E1 Layer

Internal latent-image type direct positive core/shell silver bromide emulsion	0.26
Spectral sensitizing dye (ExSS-1)	1.0×10^{-4}
Spectral sensitizing dye (ExSS-2)	6.0×10^{-5}
Gelatin	1.11
Cyan coupler (ExCC-1)	0.21
Cyan coupler (ExCC-2)	0.26
Ultraviolet absorber (ExUV-1)	0.17
Solvent (ExS-1)	0.23
Development modifier (ExGC-1)	0.02
Stabilizer (ExA-1)	0.006
Nucleation accelerator (ExZS-1)	3.0×10^{-4}
Nucleating agent (ExZK-1)	8.0×10^{-6}

E2 Layer

Gelatin	1.41
Color mixing inhibitor (ExKB-1)	0.09
Solvent (ExS-1)	0.10
Solvent (ExS-2)	0.10

E3 Layer

Internal latent-image type direct positive core/shell silver bromide emulsion	0.23
Spectral sensitizing dye (ExSS-3)	3.0×10^{-4}
Gelatin	1.05
Magenta coupler (ExMC-1)	0.16
Color image stabilizer (ExSA-1)	0.20
Compound of the Invention (III-38)	0.03
Solvent (ExS-3)	0.25
Development modifier (ExGC-1)	0.02
Stabilizer (ExA-1)	0.006
Nucleation accelerator (ExZS-1)	2.7×10^{-4}
Nucleating agent (ExZK-1)	1.4×10^{-5}

E4 Layer

Gelatin	0.47
Color mixing inhibitor (ExKB-1)	0.03
Solvent (ExS-1)	0.03
Solvent (ExS-2)	0.03

E5 layer

Colloidal silver	0.09
Gelatin	0.49
Color mixing inhibitor (ExKB-1)	0.03
Solvent (ExS-1)	0.03
Solvent (ExS-2)	0.03

E6 layer

The same as E4 layer.

E7 Layer

Internal latent-image type direct positive core/shell silver bromide emulsion	0.40
Spectral sensitizing dye (ExSS-3)	4.2×10^{-4}
Gelatin	2.17
Yellow coupler (ExYC-1)	0.51
Solvent (ExS-2)	0.20
Solvent (ExS-4)	0.20
Development modifier (ExGC-1)	0.06
Stabilizer (ExA-1)	0.001
Nucleation accelerator (ExZS-1)	5.0×10^{-4}
Nucleating agent (ExZK-1)	1.2×10^{-6}

E8 layer

Gelatin	0.54
Ultraviolet absorber (ExUV-2)	0.21
Solvent (ExS-4)	0.08

E9 layer

Gelatin	1.28
Acrylmodified copolymer of polyvinyl alcohol (modification degree: 17%)	0.17
Liquid paraffin	0.03
Latex particles of polymethyl methacrylate (average particle size: 2.8 μm)	0.05

B1 Layer

Gelatin	8.70

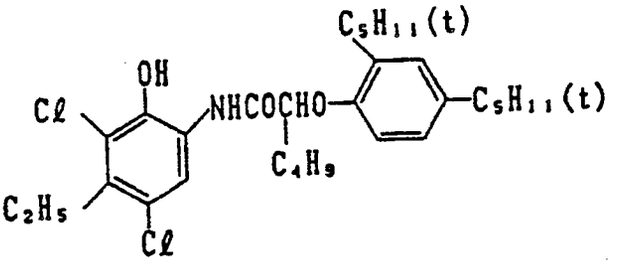
B2 Layer

The same as E9 layer.

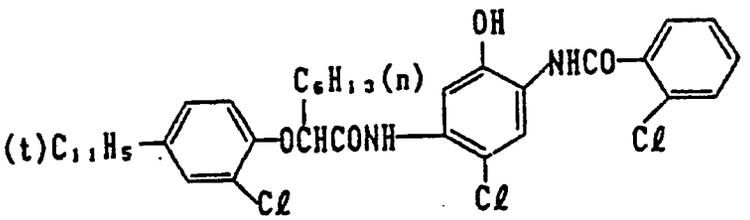
To each of the foregoing layers, a gelatin hardener ExGK-1 and a surface active agent were further added.

The compounds used for preparing the samples are illustrated below.

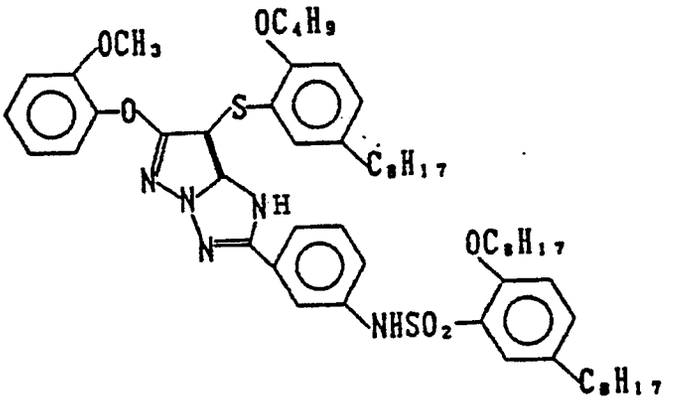
(ExCC-1) Cyan coupler



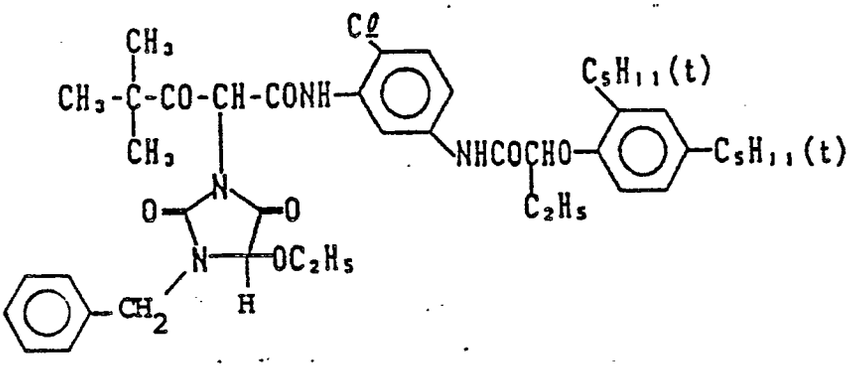
(ExCC-2) Cyan coupler



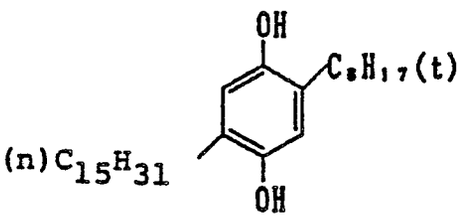
(ExMC-1) Magenta coupler



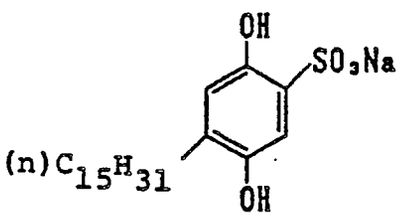
(ExYC-1) Yellow coupler



(ExKB-1) Color mixing inhibitor



(ExGC-1) Development modifier



(ExA-1) Stabilizer

4-Hydroxy-5,6-trimethylene-1,3,3a,7-tetraazaindene

(ExZS-1) Nucleation accelerator

2-(3-Dimethylaminopropylthio)-5-mercapto-1,3,4-thiadiazole hydrochloride

(ExZK-1) Nucleating agent

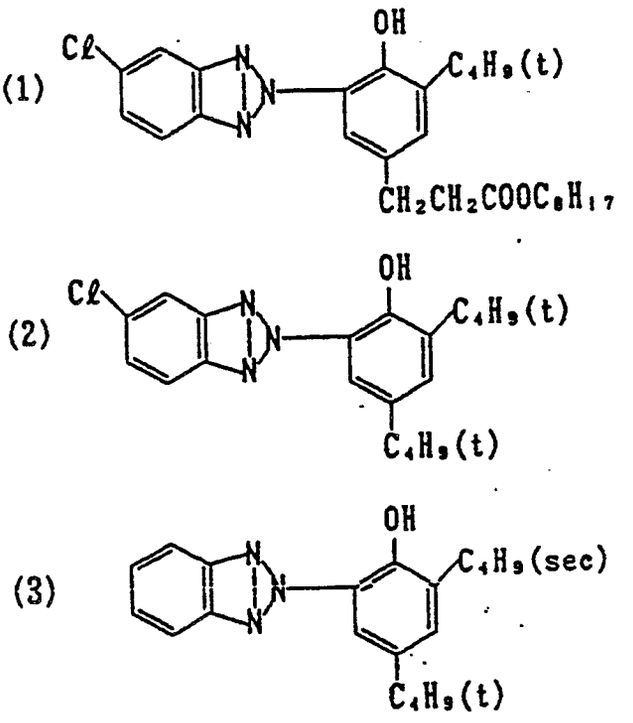
6-Ethoxythiocarbonylamino-2-methyl-1-propargylquinoliniumtrifluoromethanesulfonate

(ExGC-1) Gelatin hardener

Sodium salt of 1-hydroxy-3,5-dichloro-s-triazine

(ExUV-1) Ultraviolet absorber

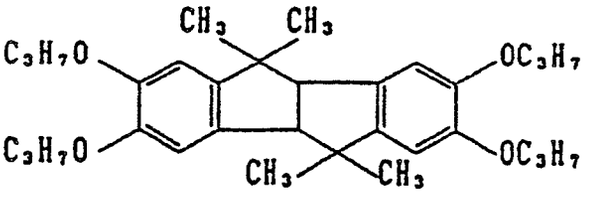
5:8:9 (by weight) of (1), (2) and (3).



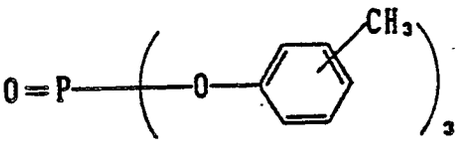
(ExUV-2) Ultraviolet absorber

2:9:8 (by weight) mixture of the foregoing (1), (2) and (3).

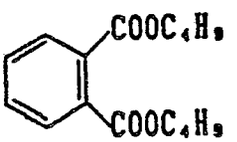
(ExSA-1) Color image stabilizer



(ExS-1) Solvent

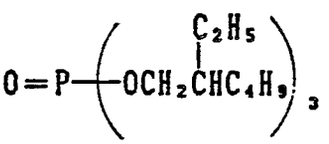


(ExS-2) Solvent



(ExS-3) Solvent

1:1 (by volume) mixture of



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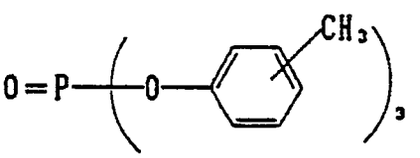
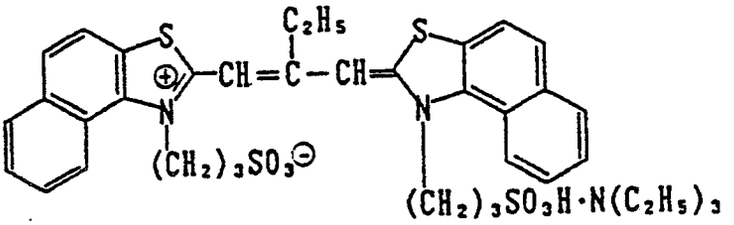


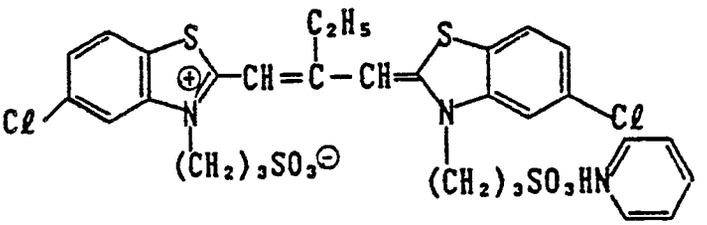
(ExS-4) Solvent

$O=P\{O\text{-}C_9H_{19}(ISO)\}_3$

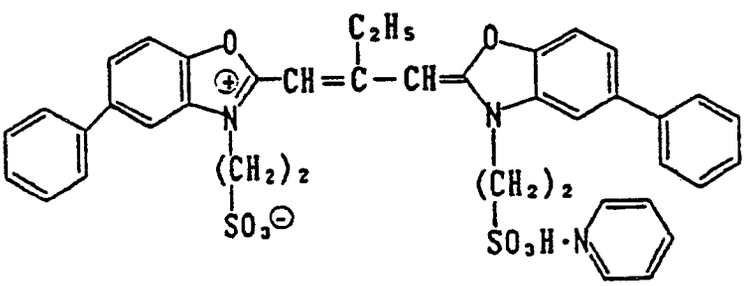
(ExSS-1) Spectral sensitizing dye



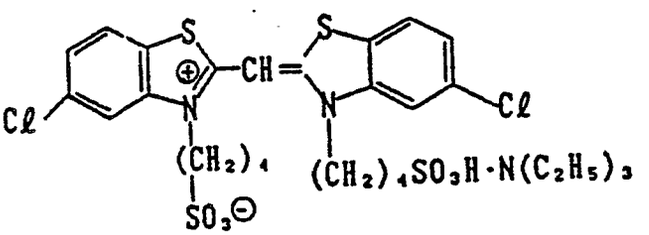
(ExSS-2) Spectral sensitizing dye



(ExSS-3) Spectral sensitizing dye



(ExSS-4) Spectral sensitizing dye



Thus prepared color photographic material was processed by the following steps. The results obtained were similar to those obtained in Example 1.

Photographic Processing A:

Step	Time	Temperature	Amount replenished
Color Development	90 sec.	38°C	300 ml/m²
Bleach-Fix	40 sec.	35°C	300 ml/m²
Water Washing (1)	40 sec.	30°-36°C	
Water Washing (2)	40 sec.	30°-36°C	
Water Washing (3)	15 sec.		320 ml/m²
Drying	30 sec.	75°-80°C	

The replenishment of washing water was performed in accordance with a countercurrent replenishing process, wherein the washing bath (3) was replenished with washing solution, and the solution overflowing the washing bath (3) was introduced into the washing bath (2), and the solution overflowing the washing bath (2) was introduced into the washing bath (1). The amount of the processing solution carried by the photosensitive material from the prebath was 35 ml/m². Accordingly, the replenishing factor was 9.1.

The composition of the processing solutions used were as follows.

Color Developer

	Tank Solution	Replenisher
Ethylenediaminetetrakismethylenephosphonic acid	0.5 g	0.5 g
Diethylene glycol	8.0 g	13.0 g
Benzyl alcohol	12.0 g	18.5 g
Sodium bromide	0.7 g	-
Sodium chloride	0.5 g	-
Sodium sulfite	2.0 g	2.5 g
N,N-diethylhydroxylamine	3.5 g	4.5 g
Triethylenediamine(1,4-diazabicyclo[2,2,2]octane)	3.5 g	4.5 g
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline	5.5 g	8.0 g
Potassium carbonate	30.0 g	30.0 g
Brightening agent (stilbene type)	1.0 g	1.3 g
Pure water to make	1,000 ml	1,000 ml
pH	10.50	10.90

The pH was adjusted with potassium hydroxide or hydrochloric acid.

Bleach-fix Bath

	Solution = Replenisher
Ammonium thiosulfate	100 g
Sodium hydrogen sulfite	21.0 g
Ammonium ethylenediaminetetraacetatoferrate(III) dihydrate	50.0 g
Disodium ethylenediaminetetraacetate dihydrate	5.0 g
Pure water to make	1,000 ml
pH	6.3

The pH was adjusted with aqueous ammonia or hydrochloric acid.

Washing water

Pure water was used as both tank solution and replenisher. The term "pure water" as used herein refers to water obtained by performing an ion exchange treatment for removing all cations other than H^+ and all anions other than OH^- from city water until all ion concentrations were reduced to 1 ppm or less.

Incorporation of both specified magenta coupler represented by the general formula (I) or (II) and the compound of the general formula (III) in the same layer ensures sufficient color developability and excellent color reproducibility, and remarkably suppresses generation of stain in unexposed areas with the lapse of time after photographic processing.

EXAMPLE 6

On a paper support laminated by polyethylene on both sides, were coated the layers described below in this order to prepare a multilayer milticolor photographic paper.

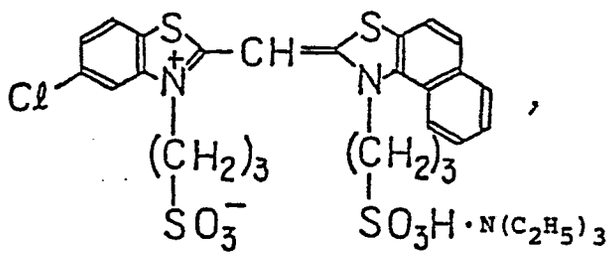
Coating compositions were prepared in the following manners.

Preparation of Coating Composition for First Layer::

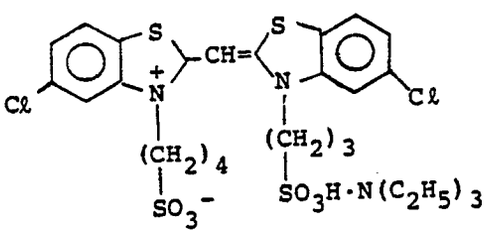
To a mixture of 19.1 g of the yellow coupler (ExY), 4.4 g of the color image stabilizer (Cpd-1) and 0.7 g of the color image stabilizer (Cpd-7), were added 27.2 ml of ethyl acetate and 8.2 g of the solvent (Solv-3) to dissolve the mixture therein. The resulting solution was emulsified and dispersed into 185 ml of a 10% aqueous gelatin solution containing 8 ml of a 10% sodium dodecylbenzenesulfonate solution. Separately, a silver chlorobromide emulsion (having a cubic crystal form, an average grain size of 0.88 μm and a variation coefficient of 0.08 in the grain size distribution, and containing bromide at the grain surface in a proportion of 0.2 mol% in the grain as a whole) was prepared, and thereto were added the blue-sensitive spectral sensitizing dyes illustrated below in equal amounts of 2.0×10^{-4} mole per mole of silver. Thereafter, the emulsion was subjected to sulfur sensitization. The foregoing emulsified dispersion and this emulsion were mixed and dissolved, and adjusted to have the coating composition for the first layer described below. Coating compositions for the second to the seventh layers were prepared in the same manner as for the first layer. In each layer, sodium salt of 1-hydroxy-3,5-dichloro-s-triazine was used as gelatin hardener.

The following compounds were used as spectral sensitizing dyes in the respective layers.

Blue-sensitive Emulsion Layer

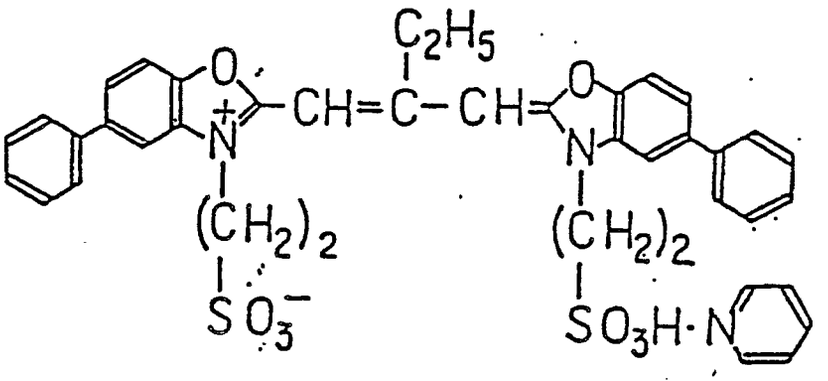


,



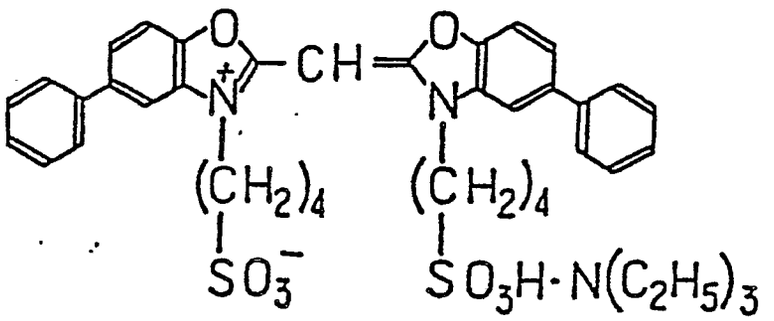
(2.0×10^{-4} mole of each compound per mole of silver halide)

Green-sensitive Emulsion Layer



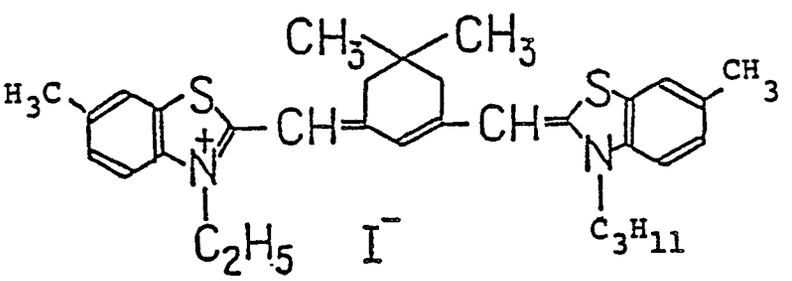
(4.0 x 10-4 mole per mole of silver halide)

and



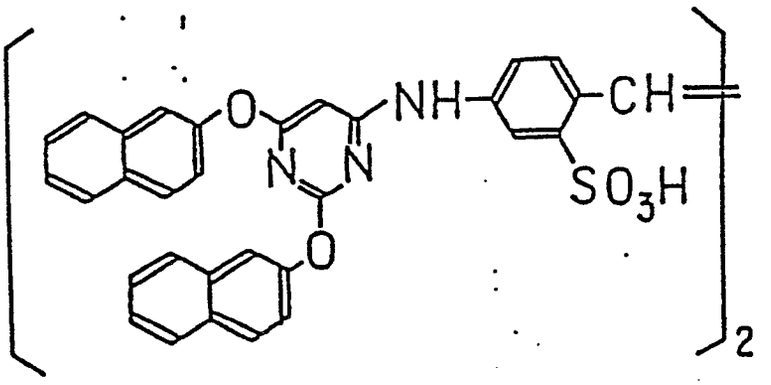
(7.0 x 10-5 mole per mole of silver halide)

Red-sensitive Emulsion Layer



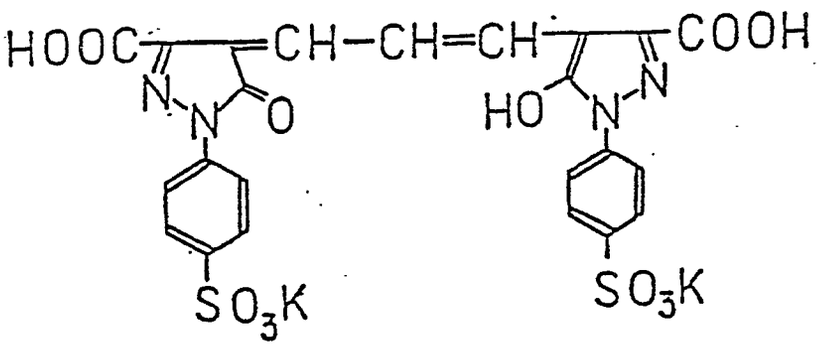
(0.9 x 10-4 mole per mole of silver halide)

In the red-sensitive emulsion layer, the following compound was additionally incorporated in an amount of 2.6 x 10^{-3} mole per mole of silver halide.

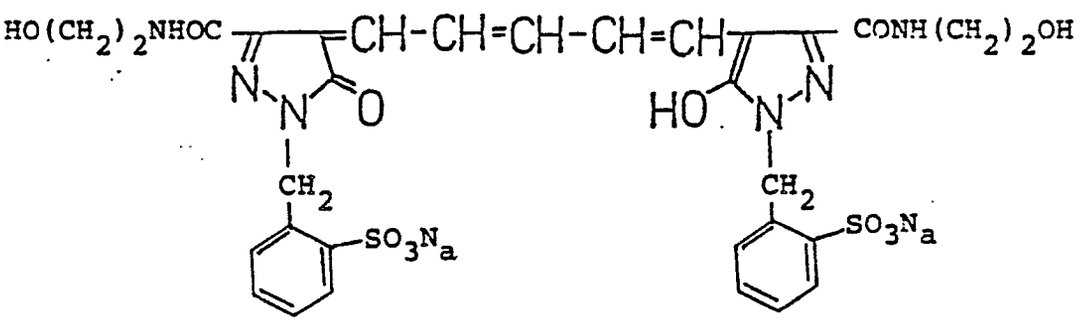


In addition to the ingredients described above, the blue-sensitive emulsion layer, the green-sensitive emulsion layer and the red-sensitive emulsion layer contained 1-(5-methylureidophenyl)-5-mercaptotetrazole in amounts of 8.5×10^{-5} mole, 7.7×10^{-4} mole and 2.5×10^{-4} mole, respectively, per mole of silver halide.

Moreover, the following dyes were added to the emulsion layers in order to prevent the irradiation.



and



Layer Structure

Compositions of the constituent layers are described below. The coverages of the ingredients used are expressed in terms of g/m^2, with the coverages of silver halides expressed on a silver basis.

(1) Support:

Polyethylene-laminated paper (which contained a white pigment (TiO_2) and a bluish dye (ultramarine) in the

polyethylene on the first layer side).

(2) First layer (Blue-sensitive layer):

The foregoing silver chlorobromide emulsion	0.30
Gelatin	1.86
Yellow coupler (ExY)	0.82
Color image stabilizer (Cpd-1)	0.19
Color image stabilizer (Cpd-7)	0.06
Solvent (Solv-3)	0.35

(3) Second layer (Color stain inhibiting layer):

Gelatin	0.99
Color mixing inhibitor (Cpd-5)	0.08
Solvent (Solv-1)	0.16
Solvent (Solv-4)	0.08

(4) Third layer (Green-sensitive layer):

Silver chlorobromide emulsion (a cubic crystal form; a 1 : 3 (by mole, based on Ag) mixture of grains having an average grain size of 0.55 µm and a variation coefficient of 0.10 in size distribution and those having an average grain size of 0.39 µm and a variation coefficient of 0.08 in size distribution; 0.8 mole% bromide, contained in individual grains as a whole, but present locally at the grain surface)	0.12
Gelatin	1.24
Magenta coupler (ExM)	0.20
Color image stabilizer (Cpd-3)	0.15
Color image stabilizer (III-1)	0.02
Color image stabilizer (I-31)	0.03
Solvent (Solv-2)	0.54

(5) Fourth layer (Ultraviolet absorbing layer):

Gelatin	1.58
Ultraviolet absorber (UV-1)	0.47
Color mixing inhibitor (Cpd-5)	0.05
Solvent (Solv-5)	0.24

(6) Fifth layer (Red-sensitive layer):

Silver chlorobromide emulsion (a cubic crystal form; a 1 : 4 (by mole, based on Ag) mixture of grains having an average grain size of 0.58 µm and a variation coefficient of 0.09 in size distribution and those having an average grain size of 0.45 µm and a variation coefficient of 0.11 in size distribution; 0.6 mole% bromide, contained in individual grains as a whole, but present locally at the grain surface)	0.23
Gelatin	1.34
Cyan coupler (ExC)	0.32
Color image stabilizer (Cpd-6)	0.17
Color image stabilizer (Cpd-7)	0.40
Color image stabilizer (Cpd-10)	0.04
solvent (Solv-6)	0.15

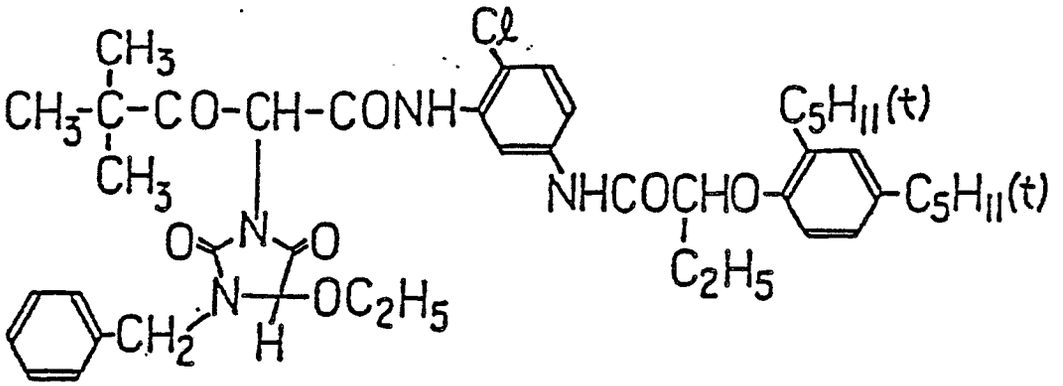
(7) Sixth layer (Ultraviolet absorbing layer):

Gelatin	0.53
Ultraviolet absorber (UV-1)	0.16
Color mixing inhibitor (Cpd-5)	0.02
solvent (Solv-5)	0.08

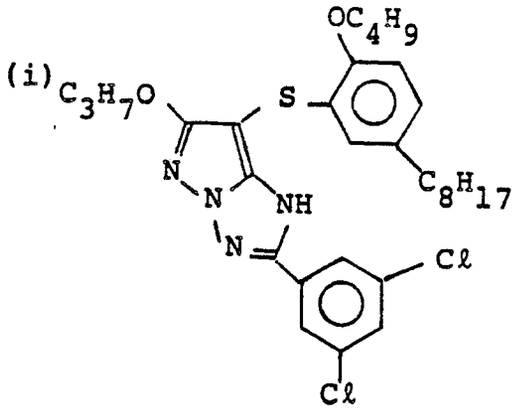
(8) Seventh layer (Protective layer):

Gelatin	1.33
Acryl-modified copolymer of polyvinyl alcohol (modification degree: 17%)	0.17
Liquid paraffin	0.03

(ExY) Yellow Coupler

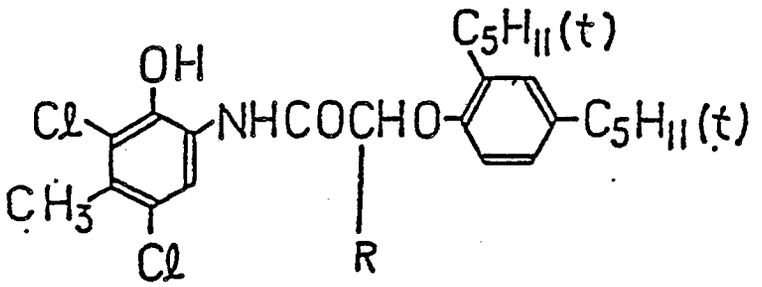


(ExM) Magenta Coupler



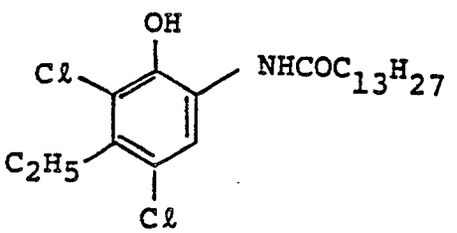
(ExC) Cyan Coupler

2:4:4 (by weight) mixture of

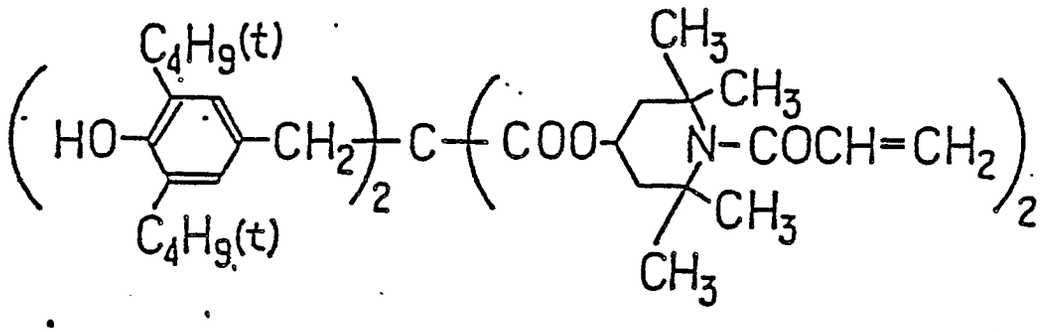


R = C_2H_5, C_4H_9

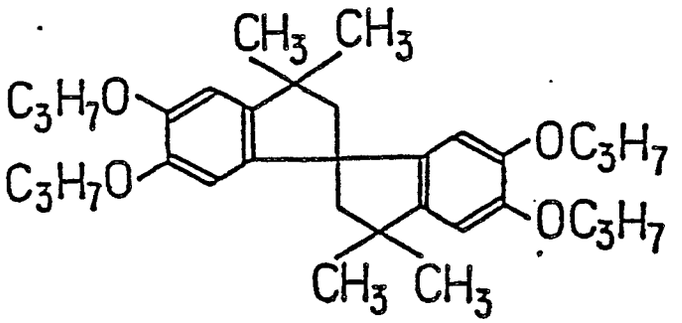
and



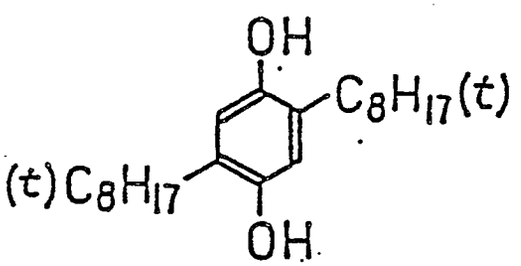
(Cpd-1) Color Image Stabilizer



(Cpd-3) Color Image Stabilizer

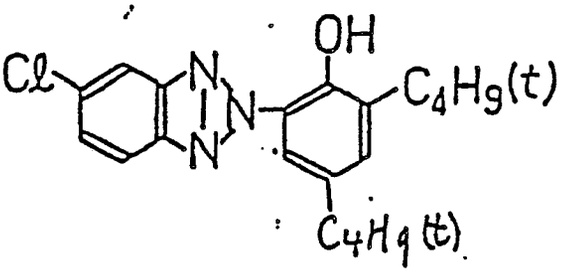


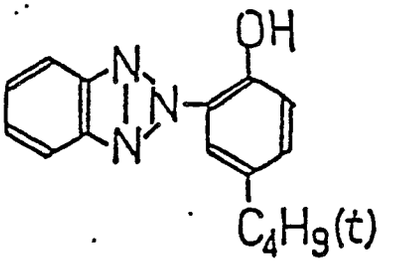
(Cpd-5) Color Mixing Inhibitor



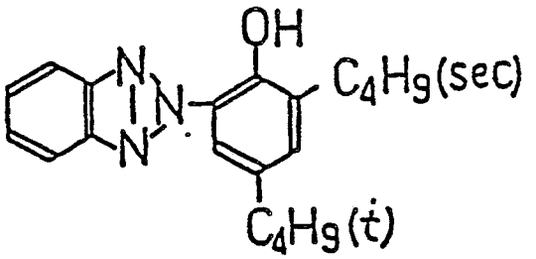
(Cpd-6) Color Image Stabilizer

2:4:4 (by weight) mixture of

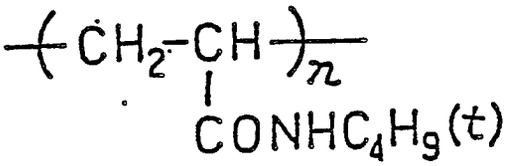




and

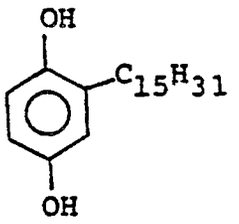


(Cpd-7) Color Image Stabilizer



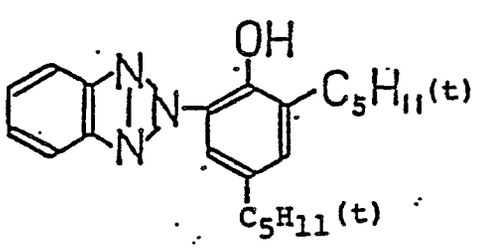
Mean molecular weight: 60,000

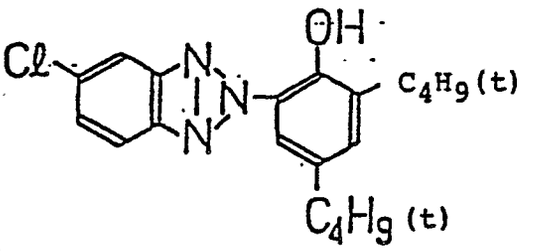
(Cpd-10) Color Image Stabilizer



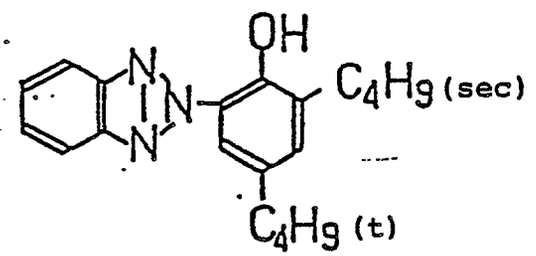
(UV-1) Ultraviolet Absorber

4:2:4 (by weight) mixture of

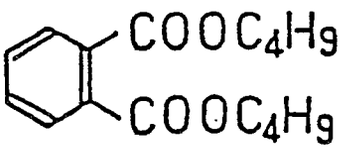




and

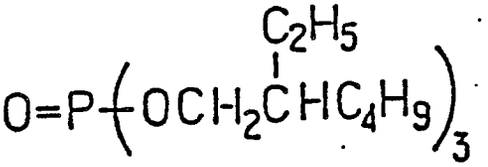


(Solv-1) Solvent

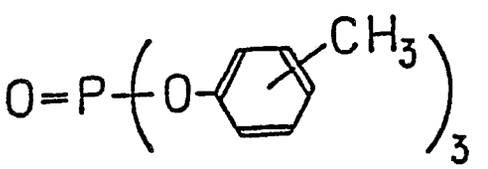


(Solv-2) Solvent

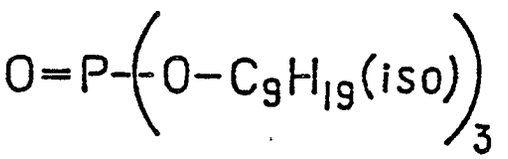
2:1 (by weight) mixture of



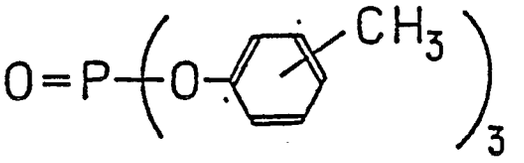
and



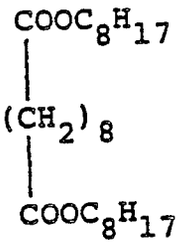
(Solv-3) Solvent



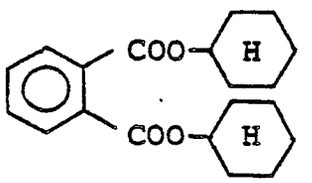
(Solv-4) Solvent



(Solv-5) Solvent



(Solv-6) Solvent



Other photosensitive materials were prepared in the same manner as the above-described one, except that the compounds of the present invention in a proportion of 10 mol% to the coupler, or/and image stabilizers were incorporated in the third layer, or the green-sensitive layer, as shown in Table 3, respectively, and subjected to the following photographic processing.

Step	Temperature	Processing Time
Color Development	35°C	45 sec.
Bleach-Fix	35°C	45 sec.
Water Washing (1)	35°C	30 sec.
Water Washing (2)	35°C	30 sec.
Water Washing (3)	35°C	30 sec.
Drying	75°C	60 sec.

Color Developer

Water	800 ml
Ethylenediamine-N,N.N′N′-tetramethylenephosphonic acid	3.0 g
Triethanol amine	8.0 g
Sodium chloride	1.4 g
Potassium carbonate	25 g
N-ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
N,N-bis(carboxymethyl)hydrazine	5.0 g
Brightening agent (WHITE X4B, produced by Sumitomo Chemical Co., Ltd)	1.0 g
Water to make	1,000 ml
pH (25° C)	10.05

Bleach-Fix Bath

Water	700 m
Ammonium thiosulfate solution (700 g/l)	100 ml
Ammonium sulfite	18 g
Ammonium ethylenediaminetetraacetatoferrate(III) dihydrate	55 g
Disodium ethylenediaminetetraacetate	3 g
Ammonium bromide	40 g
Glacial acetic acid	8 g
Water to make	1,000 ml
pH (25° C)	5.5

Washing Solution

City water treated with ion exchange resins till calcium and magnesium concentrations were each reduced to below 3 ppm (electric conductivity at 25° C: 5 μs/cm) was used.

Immediately after the photographic processing, each sensitive material was examined for yellow reflection density in the unexposed area (stain), and then allowed to stand for 20 days under the condition of 80° C and 15% RH. Thereupon, the yellow reflection densities of the unexposed areas were measured again, and thereby increases in stain with the lapse of time after the processing were determined.

The results are shown in Table 3.

Table 3

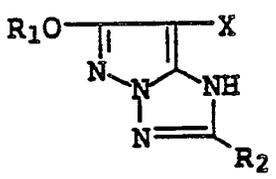
Sensitive Material	Compound of the Invention	Discoloration Inhibitor	Increment of Stain (ΔD_B)	Note
6A	-	-	+0.34	Comparison
6B	-	A-3	+0.35	"
6C	-	A-10	+0.34	"
6D	-	A-12	+0.34	"
6E	-	A-18	+0.34	"
6F	-	A-23	+0.35	"
6G	-	A-45	+0.34	"
6H	III-39	-	+0.09	Invention
6I	III-49	-	+0.12	"
6J	III-50	-	+0.15	"
6K	III-51	-	+0.15	"
6L	III-52	-	+0.13	"
6M	III-38	-	+0.08	"
6N	III-48	-	+0.10	"
6O	III-38	A-3	+0.07	"
6P	III-38	A-10	+0.06	"
6Q	III-38	A-12	+0.05	"
6R	III-38	A-18	+0.03	"
6S	III-38	A-23	+0.05	"
6T	III-38	A-45	+0.06	"

As can be seen from Table 3, the increment of stain with time after the photographic processing was considerably depressed by the compounds of the present invention. This depressing effect was particularly remarkable in the case of R = H in the general formula (III) (see the comparisons of 6H with 6I, 6J and 6K, and of 6M with 6L and 6N), and became greater by the combined use of the present compounds and various image stabilizers. The most remarkable effects upon depression of stain were accomplished by the combined use of the present compounds and the compounds represented by the general formula (IV-5).

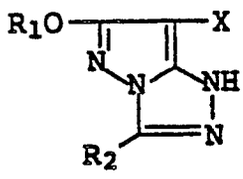
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver halide color photographic material which contains at least one coupler represented by the general formula (I) or (II-A) and at least one compound represented by the following general formula (III) in the same light-sensitive silver halide layer:

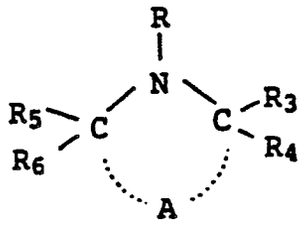


(I)



(II-A)

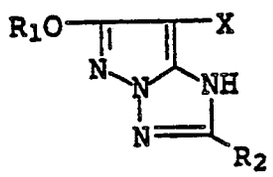
wherein R_1 represents an alkyl group, an aryl group, or a heterocyclic group; R_2 represents a hydrogen atom, or a substituent group; and X represents a hydrogen atom, or a coupling-off group.



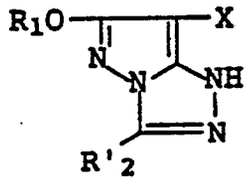
(III)

wherein R represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an oxy radical, or a hydroxyl group; R_3, R_4, R_5 and R_6, which may be the same or different, each represents a hydrogen atom, or an alkyl group; and A represents a nonmetalic atomic group necessary for forming a 5-, 6- or 7-membered ring; provided that R_3 may be linked with R_4, R_5 may be linked with R_6, R may be linked with R_3, or R_3 may be linked with A to form a 5- or 6-membered ring.

2. The silver halide color photographic material as claimed in claim 1, wherein at least one light-sensitive silver halide layer contains at least one coupler represented by formula (I) or (II-B) in combination with at least one compound represented by formula (III) above:

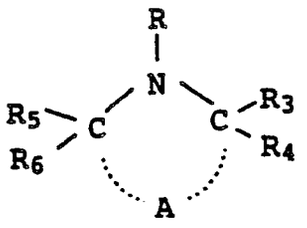


(I)



(II-B)

wherein R_1 represents an alkyl group, an aryl group or a heterocyclic group; R_2 represents hydrogen, a halogen, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, an acylamino group, an anilino group, a ureido group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, or an alkoxycarbonyl group; X represents hydrogen or a coupling-off group; when R_1 represents an alkyl group, R'_2 represents an alkyl group, an aryl group, an alkylthio group, an arylthio group or a heterocyclic thio group; and when R_1 represents an aryl group or a heterocyclic group, R'_2 represents hydrogen or an alkyl group, an aryl group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkoxycarbonyl group, a sulfinyl group, or a carbonyl group; and



(III)

wherein R represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an oxy group, or a hydroxyl group; R_3, R_4, R_5 and R_6, which may be the same or different, each represents a hydrogen or an alkyl group; and A represents a nonmetallic atomic group necessary for forming a 5-, 6- or 7-membered ring; provided that R_3 may be linked with R_4, R_5 may be linked with R_6, R may be linked with R_3, or R_3 may be linked with A to form a 5- or 6-membered ring.

3. The silver halide color photographic material as claimed in claim 2, wherein said alkyl group represented by R_2 is a substituted alkyl group substituted with a substituent selected from a sulfonamido group, an acylamino group, a sulfonamidophenylalkyl group, an acylaminophenylalkyl group, an alkylsulfonylalkyl group and a phenylsulfonylalkyl group; said alkyl group represented by R'_2 is a substituted alkyl group substituted with a substituent selected from the group consisting of a sulfonamidoalkyl group, an acylaminoalkyl group, a sulfonamidophenylalkyl group, an acylaminophenylalkyl group, an alkylsulfonylalkyl group, and a phenylsulfonylalkyl group.

4. The silver halide color photographic material as claimed in claim 3, wherein R_2 represents an alkyl group, an aryl group, an alkylthio group, or an arylthio group; and R'_2 represents a substituted alkyl group or a substituted aryl group.

5. The silver halide color photographic material as claimed in claim 4, wherein R_2 represents an alkyl group or an aryl group and R'_2 represents a substituted alkyl group.

6. The silver halide color photographic material as claimed in claim 1, wherein X represents a coupling-off group selected from a halogen atom, a carboxyl group, and a group connected to the coupling active site by an atom selected from an oxygen atom, a nitrogen atom, and a sulfur atom.

7. The silver halide color photographic material as claimed in claim 6, wherein said coupling-off group is a group connected to the coupling active site by a sulfur atom.

8. The silver halide color photographic material as claimed in claim 1, wherein at least one of R_1 and R_2 is a divalent linking group connecting said coupler to a vinyl monomer contained in a homopolymer or copolymer.

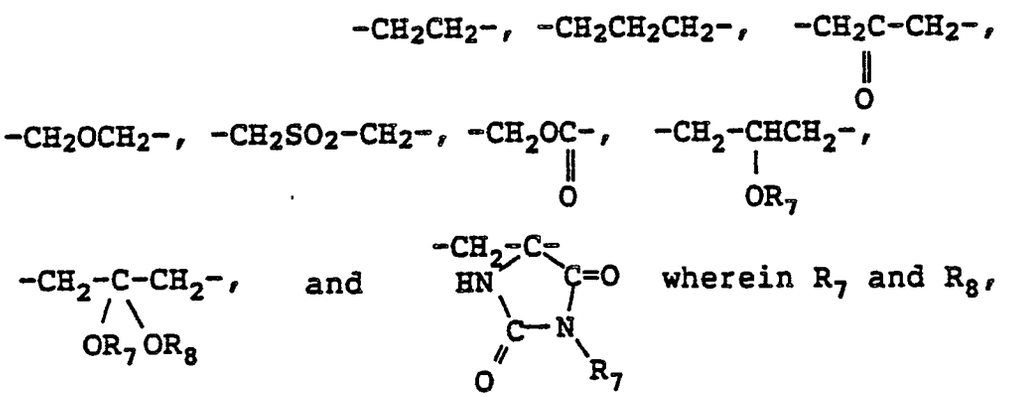
9. The silver halide color photographic material as claimed in claim 8,wherein said homopolymer or copolymer is a latex.

10. The silver halide color photographic material as claimed in claim 1, wherein said light-sensitive silver halide layer contains at least one coupler represented by formula (I) in combination with at least one compound represented by formula (III).

11. The silver halide color photographic material as claimed in claim 1, wherein said light-sensitive silver halide layer contains at least one coupler represented by formula (II-A) in combination with at least one compound represented by formula (III).

12. The silver halide color photographic material as claimed in claim 1, wherein R_1 represents a phenyl group substituted by an alkoxy group at the ortho position.

13. The silver halide color photographic material as claimed in claim 1, wherein A in formula (III) represents



which may be the same or different, each represents hydrogen, an alkyl group, an acyl group, a sulfonyl group, a sulfinyl group, or an alkoxycarbonyl group.

14. The silver halide color photographic material as claimed in claim 13, wherein at least one of R_3 and R_4, R_5 and R_6, R and R_3, or R_3 and A is linked to form a 5- membered to 6-membered ring selected from cyclohexane, cyclohexene, pyran, piperazine, piperidine and morpholine.

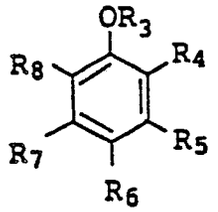
15. The silver halide color photographic material as claimed in claim 13, wherein said ring formed by A is a piperidine ring; at least two of R_3, R_4, R_5 and R_6 represent an alkyl group; and R represents hydrogen or an alkyl group.

16. The silver halide color photographic material as claimed in claim 15, wherein R represents hydrogen and each of R_3, R_4, R_5 and R_6 represents an alkyl group.

17. The silver halide color photographic material as claimed in claim 1, wherein said light-sensitive silver halide layer comprises from about 2×10^{-3} to 1 mol/Agmol of said coupler represented by formula (I) or (II-A) and from 5 to 200 mol% of said compound represented by formula (III) based on the total amount of said coupler.

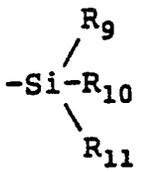
18. The silver halide color photographic material as claimed in claim 17, wherein said light-sensitive silver halide layer comprises from about 1×10^{-2} to 5×10^{-1} mol/Agmol of said coupler represented by formula (I) or (II-A) and from 10 to 50 mol% of said compound represented by formula (III) based on the total amount of said coupler.

19. The silver halide color photographic material as claimed in claim 1, wherein said light-sensitive silver halide layer further comprises at least one image stabilizer represented by (IV):



(IV)

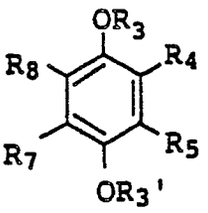
wherein R_3 represents hydrogen, an alkyl group, an alkenyl group, an aryl group, a heterocyclic group, or



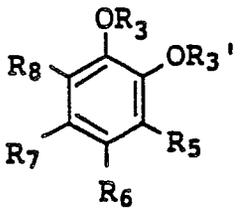
wherein R_9, R_{10} and R_{11} may be the same or different, and each represents an alkyl group, an alkenyl group, an aryl group, an alkoxy group, an alkenoxy group or an aryloxy group and R_4, R_5, R_6, R_7 and R_8, which may be the same or different, each represents hydrogen, an alkyl group, an alkenyl group, an aryl group, an acylamino group, an alkylamino group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, an aryloxycarbonyl group, a halogen atom or $-O-R_3'$, wherein R_3' has the same definition as R_3.

20. The silver halide color photographic material as claimed in claim 19, wherein said image stabilizer represented by formula (IV) is represented by formulae (IV-1), (IV-2), (IV-3), (IV-4) or (IV-5):

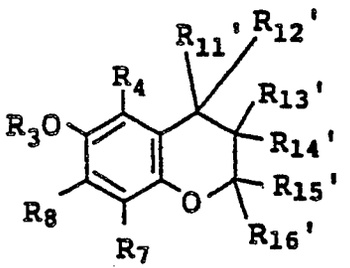
(IV-1)



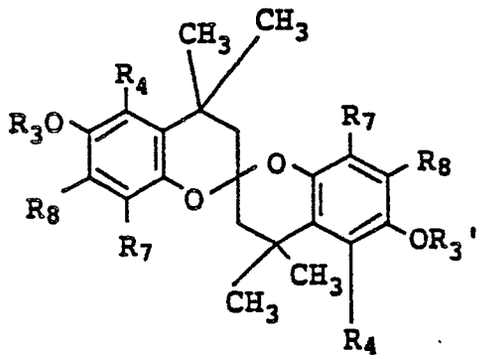
(IV-2)



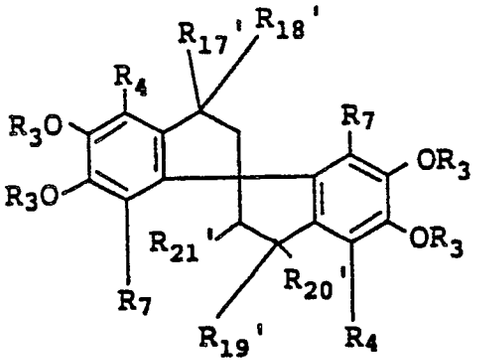
(IV-3)



(IV-4)

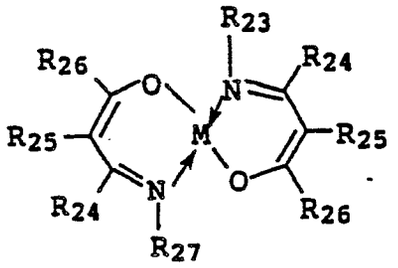


(IV-5)

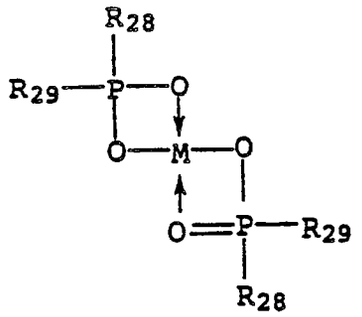


wherein R_3, R_3', R_4, R_5, R_6, R_7 and R_8 each is defined as in formula (IV); R_{11}' through R_{21}', which may be the same or different, each represents hydrogen, an alkyl group or an aryl group.

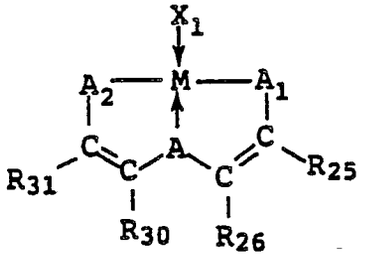
21. The silver halide color photographic material as claimed in claim 1, wherein said light-sensitive silver halide layer further comprises at least one image stabilizer selected from a metal complex represented by formulae (V-1), (V-2), (V-3) or (V-4):



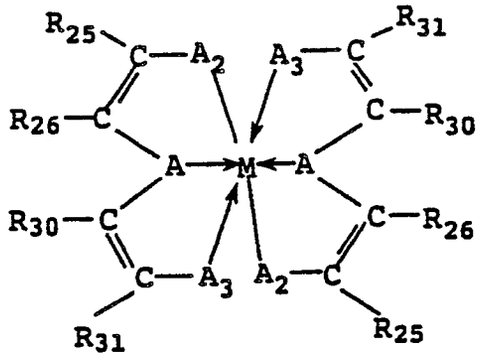
(V-1)



(V-2)



(V-3)



(V-4)

wherein M represents Cu, Co, Ni, Pd, or Pt; R_{23} and R_{27}, which may be the same or different, each represents hydrogen, an alkyl group, an aryl group, or a hydroxyl group; R_{23}, R_{24},R_{26}, R_{30} and R_{31}, which may be the same or different, each represents hydrogen, an alkyl group, or an aryl group; R_{28} and R_{29}, which may be the same or different, each represents an alkyl group, an aryl group, an alkylthio group, an arylthio group, an alkoxy group, an aryloxy group, an alkylamino group, or an arylamino group; X_1

represents H_2O or organic or inorganic amines coordinately bonded to M; A represents oxygen, sulfur or $-NR_{110}-$, wherein R_{110} represents hydrogen, an alkyl group, an aryl group, a hydroxyl group, or an alkoxy group; A_1 and A_2, which may be the same or different, each represents oxygen, sulfur, or an amino group; and A_3 represents a hydroxyl group, an alkoxy group, an alkylthio group, or $-NR_{120}R_{130}$, wherein R_{120} and R_{130}, which may be the same or different, each represents hydrogen or an alkyl group.